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Alternative Carbon Sources for Biological Denitrification of Wastewater at UBWPAD

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Alternative Carbon Sources for Biological Denitrification at Upper Blackstone Water Pollution Abatement District

A Major Qualifying Project Report

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This report is the product of an education program, and is intended to serve as partial documentation for the evaluation of academic achievement. The report should not be construed as a working document by the reader.

Professional Licensure Statement

Earning a Professional Engineering license (PE) is important to obtain for an engineering professional and is an important step in an engineer's career. Engineers are responsible for work they undertake. A PE license ensures the engineer has exceptional skills according to National Council of Examinations for Engineering and Surveying (NCEES). Before gaining a PE, one must pass the Fundamentals of Engineering exam (FE) to receive an Engineer-In-Training (EIT) license. The FE exam is a 6-hour test given in two sessions.

Each state varies in the amount of time needed working as an EIT before being eligible to take the PE exam. Each PE is required to demonstrate 15 professional development hours per year in some states. Professional development hours can be in the form of taking courses, attending seminars, publishing articles, or receiving a patent. A license can be revoked by a state if one does not abide by the code of ethics. Having a PE license revoked becomes a public record. The purpose of a PE license is to protect the public and hold engineers accountable for their work.

Every person accepts a code of ethics when entering a profession or an organization. Engineers abide by three types of codes of ethics: employer code of ethics, code of ethics for technical work with social conscience, and government code of ethics are determined through laws, codes, and regulations set by US government that must be followed in designs. Engineers need to ensure they do not have any conflicts of interest when making decisions according to the code of ethics. Having a PE license requires engineers to take personal responsibility for their work. When approving designs, the PE is ensuring the design is ethical in terms of the technical design and the effects on the people. State and federal laws do take precedence over professional ethics when it comes to making final decisions on designs. [1]

To maintain trust within the community, integrity, honor, and dignity, all members of the engineering community must abide by the principles set in the code of ethics. A PE license gives each individual engineer more responsibility and proves competence in their field of engineering.

The alternative carbon source for denitrification design would require a PE to sign off on the final design. The current design developed for Upper Blackstone Water Pollution Abatement District is preliminary and would need to be approved by a PE. Ethics were taken into consideration for the health and safety of the design.

[1] Turton, Richard. *Analysis, Synthesis, and Design of Chemical Processes*. Upper Saddle River, N.J: Prentice Hall, 2003. Print.

Design Capstone

All kinetic reactor tests were run in a 2-liter Erlenmeyer flasks with nitrogen gas released through a sparger. The nitrogen gas was sparged at a flowrate to ensure no oxygen would enter the flask and the wastewater was well mixed. A piece of Parafilm covered the top of the Erlenmeyer flask. The Parafilm had holes in it to allow nitrogen gas to be released from the system and not build up pressure. For more information on the kinetics procedure, refer to Section 3.1.

Preliminary testing consisted of a 2-hour reactor test using the set up explained prior. Temperature, pH, COD, and nitrate were measured and recorded before the carbon source was added to the reactor and again after the two hours. The preliminary test was used to determine the carbon sources that produced over 70% denitrification within two hours. The process developed was modified from the Water Environment Research Foundation (WERF).

Final testing consisted of a 3-hour reactor tests using the previously explained set up. Temperature, pH, COD, and nitrate were measured and recorded before the carbon source was added to the reactor and again after each hour. Samples for COD measurements were taken and nitrate measurements recorded every ten minutes for the first hour. After the first hour, samples were taken every half an hour. The final samples were analyzed to find the reaction rate for denitrification of the wastewater. The first slope of the data collected represents the denitrification reactions involving readily biodegradable COD. The second slope represents the slowly biodegradable COD reactions. The reactions are zero order reactions; this explains the need for a linear evaluation of the data. Final testing was modified from the procedures developed by WERF.

Based on the results from the secondary testing, a scaled-up design was developed for Upper Blackstone Water Pollution Abatement District (UBWPAD). The design can be seen in Figure 1. The biodiesel production waste was selected as the carbon source for the design.

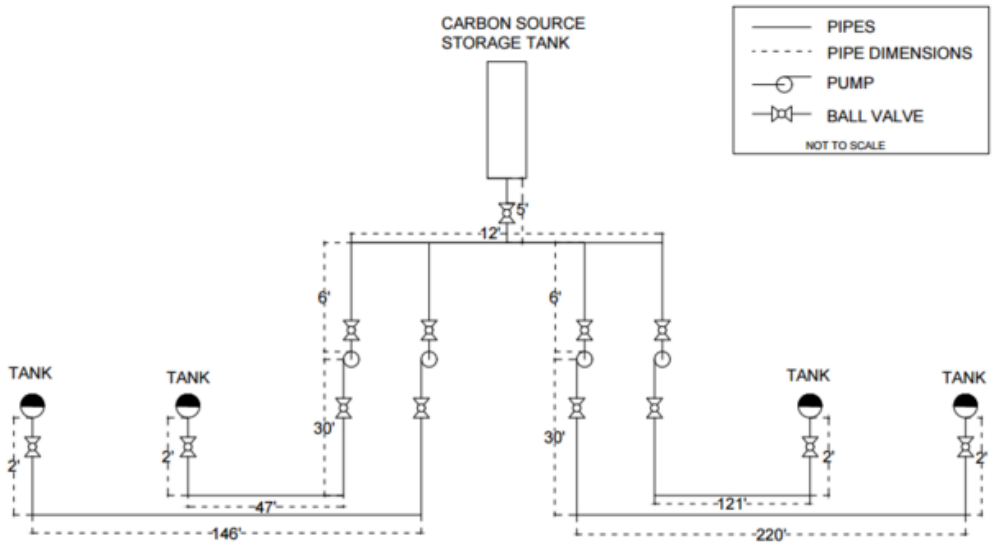

Figure 1: P&ID for Carbon Source Addition for Denitrification Design

The pipe increases ten feet in elevation before passing over the tanks and then decreasing twelve feet in elevation down to the middle of the existing biological treatment tank. The pipe outlet does not enter the wastewater in the existing tanks to avoid any blockage in the pipes. All pipes are ½ inch nominal pipe size. All valves used in the design are ball valves as they are used for on/off purposes. The piping is Schedule 40 CPVC. The pump is designed to produce a flowrate of 4.5 gal/h with a velocity of 3 m/min in the piping. The LMI Chemical Metering Pump C73 was selected based on durability, ability to pump viscous fluids, and the ability to produce the flowrate needed.

The final scaled-up design proposed minor health and safety concerns that can be easily mitigated. Over time leaking in pipes and corrosion may occur. Biodiesel production waste contains potassium hydroxide (KOH) and glycerol; these chemicals may cause some corrosion in some components over time. The pipe at the end of the system is open to the atmosphere and some off gases may enter the air when leaving the pipes. Overall, the design does not call for any special hazard precautions to be set in place.

Abstract

The purpose of this project was to determine alternative carbon sources for biological denitrification at Upper Blackstone Water Pollution Abatement District (UBWPAD). Carbon sources tested consisted of various wastes: Micro-C, beverage waste, unrefined biodiesel production waste, sugar production waste, Dow Chemical waste, Elite Chemical waste, and deicer fluid. The carbon sources were evaluated for their denitrification rate in a kinetic reactor tests; those reaching 70% or more in denitrification extent were subjected for final testing. A design for the addition of the alternative carbon sources to the denitrification process was developed for UBWPAD.

Acknowledgements

The completion of this project would not have been possible without the help and support from our sponsor, Upper Blackstone Water Pollution Abatement District (UBWPAD), and our advisers: Professor Kmiotek, Professor Bergendahl, and Professor Bates. Mark Johnson from UBWPAD was always helpful with obtaining information about the wastewater treatment plant's operation. Debra LaVergne from UBWPAD helped with obtaining samples from the aeration tanks and data about the process at UBWPAD.

Our advisers were always helpful with suggesting various approaches for our experiment and analyzing our data. They helped to push our project in the right direction. A special thank you to UBWPAD, Professor Clark, Ron Eastman at Garelick Farms, DOW Chemical, and Elite Chemical for contributing the various carbons sources evaluated.

Executive Summary

The research discussed in this report is to assist Upper Blackstone Water Pollution Abatement District (UBWPAD) in the selection of a new carbon source for denitrification of wastewater. Ammonification and nitrification are both common processes in the environment. Bacteria converts ammonium to nitrates, causing nitrates to form in wastewater. Denitrification occurs under anoxic conditions to remove nitrates from water by forming nitrogen gas. Wastewater needs to be treated before releasing it back into a water source such as a river, lake, or ocean to prevent any harmful substances from reentering the water source. Wastewater undergoes primary and secondary treatment before being released into a water source. Biological denitrification in secondary treatment was the main focus of the study presented in this report.

To ensure the wastewater meets regulations when returned to the environment, the wastewater needs to undergo effective treatment including denitrification. Various organics have been known to efficiently function as carbon sources for biologically reducing total nitrogen concentration in wastewater. UBWPAD seasonally uses Micro-C 2000A as the carbon source for denitrification. Micro-C is a glycerin based chemical. Other carbon sources investigated included various industrial wastes. Repurposing organic industrial waste for use as a carbon source is both a sustainable and cost effective opportunity.

Micro-C was tested as a baseline in these experiments to compare with other potential sources. Alternative carbon sources initially considered for experimentation included wastes from the production of beverages, breweries, dairy products, wine and alcoholic beverages, biodiesel production, sugar, municipal solid waste landfill leachate, and chemical manufacturing. Not all of these potential organics were able to be obtained or reproduced and could not be studied in further detail. The carbon sources not obtained or reproduced were as follows: brewery waste, winery and alcoholic beverage waste, and waste from a municipal solid waste landfill.

Each carbon source was tested for its chemical oxygen demand (COD), nitrate levels, temperature, and pH and further evaluated in a kinetic reactor test. New samples of wastewater were filtered and then dried at 105 degrees Celsius to determine the mass of mixed liquor suspended solids (MLSS). These values were used to calculate the denitrification rates of each carbon source. The COD test used standard COD vials reading up to 900 mg/L. Samples were diluted to obtain a COD reading of less than 900 mg/L. Nitrate concentrations were measured with a nitrate probe. The temperature was measured with a thermometer and pH was measured with a pH probe and meter. The kinetic reactor test approach consisted of a preliminary test and a final test. The preliminary test was a 2-hour test where samples were taken at the beginning and

end of the two hours. The reactor was anoxic and well mixed using nitrogen gas. The final test had the same reactor set up and was a 3-hour long test with samples taken throughout the duration.

Each carbon source was evaluated in the preliminary test except for the dairy waste. Dairy waste was found to be not easily obtainable, variable in COD and content, and would lead to more odor control needed at UBWPAD. Corn syrup was suggested by UBWPAD after our initial tests were completed. The percent of nitrogen removal for corn syrup, a beverage waste, was determined after the first two hours of the final test. Nitrogen removal for Micro-C, beverage waste, unrefined biodiesel production waste, sugar production waste, Dow Chemical waste, Elite Chemical windshield wiper fluid waste, and deicer fluid were 80.6%, 79.8, 83.1%, 86.2%, 79.8%, 52%, and 43.4%, respectively.

Carbon sources were selected to be tested in the final test if the source managed to reduce nitrogen by 70% in the denitrification kinetics test. The final test consisted of taking the same readings from samples as in the first test. Samples were taken in the beginning, every ten minutes for the first hour, and every half an hour for the last two hours. For all final tests, the initial COD of the carbon source did not fluctuate more than 650 mg/L. The changes in the source COD should not pose any issues for UBWPAD, though UBWPAD will need to determine how this will affect the treatment processes post denitrification.

Temperature in all of the final test reactors did not surpass room temperature. No significant increases in temperature occurred throughout the experiment. The pH for the Micro-C test was 6.90-7.34 from beginning to end of the final test. The ideal range for wastewater pH is between 7-7.5. The next three tests began at a pH greater than the ideal pH for a system: corn syrup ranged from 7.53-7.98; biodiesel waste ranged from 7.63-8.4; the sugar solution's pH ranged from 7.54-8.08. Glycerin did surpass the ideal pH range as well with a pH change from 6.66-7.66. UBWPAD would need to decide whether or not these pH changes are acceptable on a day to day basis of running the plant.

UBWPAD was recently operating with 30 minute detention times in the anaerobic tanks. All final batch reactor experiments produced nitrate concentrations below 2 ppm within a half hour. This illustrated all carbon sources as effective for denitrification. The carbon sources with the greatest denitrification rates, above –0.050 kgN/kgVSS/d, were considered for design and cost analysis.

Micro-C had a reaction rate of –0.053 kgN/kgVSS/d for the first 50 minutes of the reactor test. Beverage production waste, corn syrup, had a denitrification rate of -0.057 kgN/kgVSS/d over 40 minutes. Corn syrup denitrifies faster than Micro-C; the tank size is not of concern for

this source. Biodiesel production waste had the fastest reaction rate of -0.103 kgN/kgVSS/d. The denitrification process occurred in 20 minutes. Sugar solution had the slowest reaction rate of -0.039 kgN/kgVSS/d occur over 80 minutes. The reaction time for sugar was the slowest and further tests would have to be done to ensure higher levels of nitrate can be depleted within the detention time. DOW Chemical, glycerin, had a reaction rate of -0.052 kgN/kgVSS/d, similar to Micro-C. The reaction completed within the first 40 minutes of the kinetic reactor experiment.

Potential injection system designs utilizing these alternative carbon source for denitrification were considered assuming an average 30MGD wastewater flow and year round influent concentration of 8 ppm nitrate. The carbon sources with denitrification rates over –0.05 kgN/kgVSS/d were corn syrup, DOW chemical, sugar solution, and biodiesel production waste. This is a longer time period and higher nitrate concentration than UBWPAD generally experiences. The general design consists of a storage vessel, pumps, and piping to each anaerobic tank. Biodiesel production waste was chosen as the final and most effective carbon source to recommend. The design of corn syrup, sugar solution, and glycerin called for significantly higher volumes for storage, larger pumps to operate, and more frequent and larger shipments. Biodiesel production waste required about 3,000 gal/month which can be stored in vessels UBWPAD already has on-site. The design incorporating of biodiesel production waste was more feasible than the other potential carbon sources.

The LMI Series C Chemical Metering Pump C73 was selected for the design because it is durable and can handle high viscosity fluids. The C73 model can handle a flow rates up to 8 GPH; the required biodiesel waste flow rate is within this range, averaging around 4 GPH. The average input power at max speed is 44 watts.

Chlorinated polyvinyl chloride (CPVC) was selected for the piping material because CPVC is not affected by changes in outside temperature or corrosive solutions. The piping will exit the chemical holding tank, flow through a series of valves and enter the pump. There will be four pumps, one for each anaerobic tank with one pipe coming from each. The flow will exit each pump and the pipes will run at an elevation increase of ten feet to clear the walk area and then will reduce elevation back down twelve feet. Each pipe stops in the middle of the beginning of an anaerobic tank and hangs two feet into the tank, above the wastewater level to release the biodiesel production waste. The pipe design has a negligible pressure drop of 0.17 ft. due to the material of the pipe and low flow rate. All pipes in the system are 0.5" in nominal pipe size. The overall design can be seen in Figure 2.

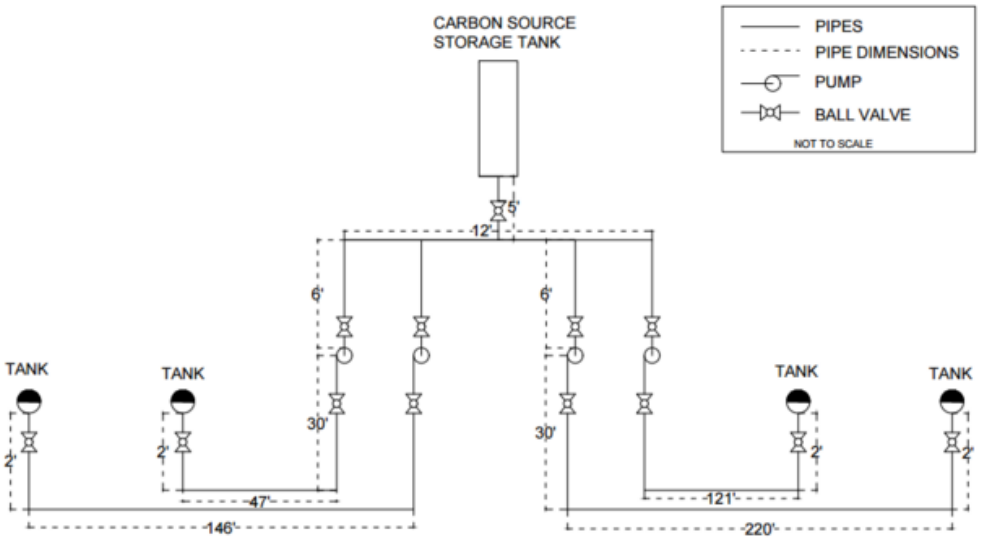

Figure 2: P&ID of Carbon Source Addition for Denitrification

Health and safety were considered when selecting carbon sources and materials for the design. Carbon sources primarily composed of methanol were not considered due to safety concerns with having the chemical onsite. If methanol is used at the plant, eye wash stations would need to be installed and there would need to be an on-site firefighter at the plant. Carbon sources were also analyzed for their impact on the Blackstone River once the treated water is discharged. Ethylene glycol was eliminated as it has been linked to reproductive issues in females, and milk waste was eliminated due to its variable and unknown composition. Design materials were evaluated based on their ability to handle a chemical with a high pH, since the biodiesel waste is basic. This will prevent corrosion and degradation of the materials.

The biodiesel production waste injection system has an approximate total capital cost of $6,600 for all equipment. This includes costs for 735 feet of CPVC piping, 13 ball valves, and four LMI Series C Chemical Metering C73 Pumps. Storage vessels were not included in this financial analysis as UBWPAD already has one 2,000-3,000 gallons plastic vessel that is sufficient, as well as two 200-300 gallons metal encased plastic vessels for additional storage. Two potential biodiesel production waste suppliers are Northeast Biodiesel and Mass Biofuels. These locations are 64.1 and 41.7 miles away from UBWPAD, respectively and the cost of transportation for each will have to be determined. Cost of biodiesel waste will have to be negotiated between the manufacturer and UBWPAD.

Based on our studies, we recommend using biodiesel production waste as an alternative carbon source for biological denitrification at UBWPAD. The pricing and availability of biodiesel

waste will need to be negotiated between the company and UBWPAD. Companies in the area producing biodiesel waste are Northeast Biodiesel and Mass Biofuels.

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1. Background

1.1. Wastewater Treatment

Wastewater treatment is an integral part of how water is reused. Wastewater contains harmful pathogens, organics, and nutrients, as well as other contaminants. Therefore, it is important to treat wastewater before discharging to a water body or directing the treated wastewater to a reuse application. Prior to the Federal Water Pollution Control Act of 1972, now known as the Clean Water Act, federal wastewater regulations had not been promulgated. [2] In addition to the foul odor it produced, the untreated water led to contaminants floating on rivers igniting, such as the Cuyahoga River in northeast Ohio.[3] The incident made clear that water must be treatment before disposal.

Treated wastewater has several applications: agricultural uses, golf course fertilizing and irrigation, and lawn irrigation. In many cases, treated wastewater is discharged to rivers. Treated wastewater from the Upper Blackstone Water Pollution Abatement District (UBWPAD) is discharged to the Blackstone River. The treated wastewater provides a large percentage of the total volume of the Blackstone River during dry conditions in the summer.

The process of wastewater treatment at a municipal plant involves three main treatment levels: primary treatment, secondary treatment and tertiary treatment. Appendix G displays an AutoCAD diagram of the entire wastewater treatment system at UBWPAD. Primary treatment involves sand and grit removal and primary clarification. The main purpose of primary treatment is to remove settling or floating pollutants. Sludge is produced from primary treatment and needs to be disposed. Secondary treatment involves aeration and secondary clarification. The goal of secondary treatment is to remove soluble biological oxygen demand (BOD) not removed during primary treatment, and to filter the water of suspended solids.[4] During tertiary treatment, water is disinfected and bacteria are inactivated. Tertiary treatment can be completed by a variety of methods: chlorination, ozonation, or ultraviolet light disinfection. An important step of tertiary treatment is denitrification, to remove nitrate from the water by converting it to N_2 gas. During denitrification, the treated wastewater enters an anoxic chamber as a homogeneous liquid. Debris, sludge, and other solids have already been removed along with 90% of organic matter during both the primary and secondary treatment steps.

[2] Davis, M., & Masten, S. (2004). Wastewater Treatment. In *Principles of Environmental Engineering and Science*. New York, NY: McGraw-Hill.
[3] Ibid.
[4] Ibid.

Nitrogen generally takes the form of nitrate or nitrite in secondary-treated wastewater. It is important to remove excess nitrogen in water; if it is not removed, it can have harmful effects on both human and aquatic life. High concentrations of nitrogen in water are associated with formation of algae blooms, which deplete the water body of oxygen and form dead zones.[5] Additionally, in the case of a cyanobacteria (blue-green algae) bloom, when the cells die, they may release harmful toxins into the water that can disrupt humans' nervous systems, kidneys and livers if ingested.[6] Furthermore, high nitrate levels in water are associated with blue baby syndrome.[7] Nitrogen removal in wastewater is especially important if wastewater is discharged into a salt water body, since nitrogen is the limiting nutrient in salt water. For fresh water bodies phosphorus is the limiting nutrient. In the case of the UBWPAD, the Blackstone River eventually discharges to Narragansett Bay, thus nitrogen and phosphorus removal is imperative.[8]

1.2. Nitrogen in Wastewater

Nitrogen is a common element found in atmospheric, terrestrial, and aquatic environments. Nitrogen is often found in wastewater because of two chemical processes: ammonification and nitrification. Ammonification is the conversion of reactive, organic nitrogen to ammonia and reactive hydroxide. Equation 1 displays the chemical equation of ammonification.[9]

Equation 1: The Chemical Equation of Ammonification

$$RNH_2 + H_2O + H^+ \rightarrow ROH + NH_4^+$$

Nitrates (NO_3^-) are formed through the process of nitrification. Ammonium (NH_4^+) is oxidized and then converted to NO_3^- by a group of bacteria, known as ammonium oxidizing bacteria (AOB). AOB are aerobic chemoautotrophs, meaning that they extract energy from the oxidation of inorganic compounds and use inorganic carbon for cell synthesis. Other byproducts

[5] Constantine, T. (2008, February 19). An Overview of Ammonia and Nitrogen Removal in Wastewater Treatment. Retrieved September 16, 2015.
[6] Ibid.
[7] Ibid.
[8] Upper Blackstone Water Pollution Abatement District versus United States Environmental Protection Agency (United States Court of Appeals For the First Circuit August 03, 2012) (Dist. file).
[9] Theis, T. & Hicks, A. (2012) *Methanol Use in Wastewater Denitrification.* Exponent, Inc. Retrieved from <http://www.methanol.org/getdoc/74efb789-8095-4313-be84-38f6ae0df142/Exponent-Methanol-Denitrification-Report-July-2012.aspx>

formed during nitrification are water, bacteria, and carbonic acid. Equation 2 displays the chemical equations of nitrification which includes the oxidation and cell synthesis reactions. [10]

Equation 2: The Chemical Equation of Nitrification

$$NH_4^+ + 2O_2 + 2HCO_3 \rightarrow NO_3^- + 2CO_2 + 3H_2O$$

Normal nitrogen concentrations in wastewater range from 20-70 mg/L. [11] Roughly 60%-70% of the nitrogen acts as ammonia-nitrogen, 30%-40% acts as organic nitrogen, and less than 1% acts as nitrite and nitrate nitrogen. The alkalinity consumed during nitrification may lower the pH of wastewater to harmful rates, especially when the original pH value was below 6.8. The optimal nitrification rate occurs when the pH of the system is between 7.5 and 8, but will operate effectively in the range of 7–7.8.[12]

1.3. Denitrification of Wastewater

Denitrification is a biological process that removes nitrates from water. The process is performed under anoxic conditions. Organic material removes nitrates by nitrate dissimilation, where nitrates accept an electron instead of oxygen; therefore, an anoxic environment is needed for effective denitrification.[13] Equation 3 displays the chemical equation of denitrification with methanol.

Equation 3: The Chemical Equation of Denitrification

$$5CH_3OH + NO_3^- \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^-$$

During denitrification, nitrates are converted into nitrogen gas and removed from the wastewater. Other minor byproducts are formed depending on the carbon source added. The carbon source added acts as the electron donor is needed to perform denitrification because all of the organic matter has already been consume aerobically. Common carbon sources include methanol, ethanol, etc. Different carbon sources produce different rate of denitrification. For example, ethanol is more efficient in denitrification than methanol.[14]

In order for denitrification to go to completion, the wastewater must be at an appropriate pH and temperature. The higher the temperature, the higher the denitrification rate. The optimum

[10] Theis, T. & Hicks, A. (2012) *Methanol Use in Wastewater Denitrification.* Exponent, Inc. Retrieved from <http://www.methanol.org/getdoc/74efb789-8095-4313-be84-38f6ae0df142/Exponent-Methanol-Denitrification-Report-July-2012.aspx>
[11] Ibid.
[12] Ibid.
[13] Ibid.
[14] Ibid.

denitrification rate occurs at 40 degrees Celsius and the preferred pH of wastewater is between 7 and 8.[15]

1.4. Wastewater Treatment at Blackstone

The UBWPAD is a large wastewater treatment plant in Massachusetts servicing the greater Worcester communities along with fourteen others.[16] The plant's permitted average monthly flow is 56 million gallons per day (MGD) and the plant was designed for an average daily flow of 45 MGD. The system is carbon limited at certain times of the day. The treatment plant bypasses some carbon from the beginning of the system to the denitrification process during the higher carbon content periods of the day. Low flow and high temperatures also limit the system. If the flow of wastewater is too low, a lower dosage of carbon is needed. Furthermore, denitrification is a seasonal procedure. Additional bacteria is present in the summer and spring seasons because bacteria thrive in high temperatures. For this reason, more carbon is needed in spring and summer seasons for complete denitrification compared to winter and fall seasons. [17]

The untreated water enters the plant at its headworks facility and continues on to the primary settling tanks. After the primary settling tanks, the wastewater continues on to open tanks and undergoes an anaerobic process. The denitrification process and phosphorus removal is performed in the aeration tanks before entering the final settling tanks. UBWPAD does not favor the phosphorus or nitrogen removal because they are both important to the treatment process. The treated water enters the river and the remaining organics are sent to the incinerator to burn in the thickening building, where all the sludge is processed. Some of the microorganisms from the settling tank are returned to the beginning of the anaerobic process to consume more microorganisms. The process can be seen in Appendix F.[18]

The UBWPAD has a dynamic system that can be run in multiple ways; the most common system used there is the biological nutrient removal (BNR) process and when there are occasions of high flow rates the step feed mode is then temporarily used. The primary tanks are used to settle sand and grit, and the flow measurement is taken for supercritical and subcritical flows. Activated sludge is also present in the primary tanks to begin phosphorous removal. The activated

[15] Wastewater handbook. Conditions for denitrification. Retrieved on October 29, 2015. <http://www.wastewaterhandbook.com/documents/nitrogen_removal/431_NR_denitrification_prerequisites.pdf?
[16] Upper Blackstone Water Pollution Abatement District. (n.d.). *Home*. Retrieved from Upper Blackstone Water Pollution Abatement District: http://www.ubwpad.org/
[17] Mark Johnson, Personal Correspondence, September 4, 2015.
[18] Ibid.

sludge is found within the four tanks seen above to transform nitrate into nitrogen gas. The transformation occurs by going through the anaerobic, aerobic, and oxygenated processes.[19]

1.4.1. Denitrification Process at Blackstone

Currently, UBWPAD uses Micro-C™ 2000-A as its source of carbon in denitrification. Micro-C™ 2000-A is a glycerin-based liquid chemical that donates the necessary electron to bacteria in order to complete the reaction. Table 1 contains important data and properties of the Micro-C™ 2000-A.[20]

Micro-C is a glycerin ($C_3H_8O_3$) based, man-made product from Environmental Operating Systems (EOS). This carbon source is non-flammable and has maintained a stable and affordable price around $0.43/L. Micro-C is water-soluble and has a pH of 5.8 at 25 degrees Celsius and a freezing point of -20 degrees Celsius.[21] The COD of Micro-C is 1,105,000 mg/L. These properties are all desirable and make the chemical easier and safer to handle, store, and utilize.[22]

Table 1: Properties of Micro-C[23]

Product	Results	Unit
Glycerin	71.2	%
COD Value	1,105,000	mg/L
Freezing Point	< 0	°F
Viscosity @ 20 °C	45	cP (centipoise)
Methanol Content	0-0.06	% w/w
Ash	5.5	%
pH	9.4	SU
Specific Gravity	1.233	-
Color	Golden	-
Odor	Pass	-

At the facility, Micro-C is transferred from a container where is it then delivered to the anoxic zones of tank 2 and tank 3 via pumps. A hose pump, or a positive displacement pump, is used to control flow. Each tank receives 250 gallons per day, totaling 500 gallons per day. During

[19] Mark Johnson, Personal Correspondence, September 4, 2015.
[20] Environmental Operating Solutions, MicroC Premium Carbon Sources. (2006). Environmental Operating Solutions Inc., Bourne. Retrieved September 5, 2015. <http://microc.com/product/index.htm>
[21] Cargill. (2013, June 20). IsoClear® 42% High Fructose Corn Syrup. Retrieved February 4, 2016, from https://www.cargillfoods.com/wcm/groups/internal/@cseg/@food/@all/documents/document/na3014966.pdf
[22] Cherchi, C et. al., (2009). Implication of Using Different Carbon Sources for Denitrification in Wastewater Treatments.Water Environment Research, Volume 81, Issue 8.
[23] Environmental Operating Solutions, MicroC Premium Carbon Sources. (2006). Environmental Operating Solutions Inc., Bourne. Retrieved September 5, 2015. <http://microc.com/product/index.htm>

certain periods of the year, bypassed carbon from the inlet stream may be used. A different carbon source is needed because a denitrification rate of 5 mg/L is not desirable.

A full-scale pilot study with Micro-C for denitrification is in place and may be substituted with other carbon sources as well. Micro-C is currently used because it does not require explosion-proof buildings, flammable storage tanks, or other safety requirements. Using Micro-C saves a significant amount of money. Micro-C is an efficient electron donor and is derived from renewable resource in the United States. Compounds with more electronegativity are usually better electron donors. The Micro-C used at UBWPAD has a glycerol base. The methanol compound is less complex and is less polar than the Micro-C.[24]

There are many safety concerns to consider before selecting new a carbon source. For example, methanol has several hazardous risks associated with handling it. According to the methanol MSDS, this chemical is an irritant when in contact with the skin, eyes, inhaled, or ingested. Prolonged overexposure may result in death. Methanol is also highly flammable in liquid or soluble form as well as explosive in vapor form. Protective storage and handling equipment is required.[25] To use methanol at UBWPAD, an on-site firefighter must constantly be on standby and eyewash stations must be readily available. This can be very expensive for the facility. This makes Micro-C a better much fit for aiding in denitrification of wastewater than methanol.

1.5. Alternative Carbon Sources

The following carbon sources were assessed for their effectiveness at removing nitrate from wastewater at UBWPAD. Each carbon source was analyzed based on the composition, COD, cost, freezing and boiling temperatures and pH.

1.5.1. Micro-C

UBWPAD currently uses the chemical Micro-C 2000A as an additional carbon source for denitrification. The cost of this source is higher than desired to produce the desired results, therefore, other potential sources are being sought. The opportunity to use waste from other companies is expected to be the most beneficial option for economic and environmental reasons.

[24] Environmental Operating Solutions, MicroC Premium Carbon Sources. (2006). Environmental Operating Solutions Inc., Bourne. Retrieved September 5, 2015. <http://microc.com/product/index.htm>
[25] Material Safety Data Sheet Methyl alcohol MSDS. (2013, May 21). Retrieved October 27, 2015.

1.5.2. Beverage Waste

The beverage industry produces sodas and seltzer waters. Beverage waste is primarily composed of corn syrup and high fructose corn syrup diluted by water. High fructose corn syrup (HFCS) is composed of fructose, glucose, sugars and polysaccharides (glucose chains).[26] The pH of corn syrup ranges from 3.3 to 4.5 and it has a theoretical COD (TCOD) value of 1.067 g TCOD/ g substrate. A 1000 kg tote of corn syrup can cost from $733.15-$845.71 depending on the concentration. HFCS syrup must be stored at higher temperatures between 27-32 degrees Celsius to prevent crystallization. Thus, pipes used for transporting high concentrations of beverage waste such as HFCS must be heated so the syrup does not solidify.[27]

The Water Environment Foundation tested HFCS as a carbon source for denitrification. The study concluded that HFCS is an effective denitrifying agent, and saw decreases in nitrate as nitrogen from 8.8 mg/L to 2.7 mg/L. However, the Water Environment Foundation identified three main challenges to using HFCS for denitrification:[28]

1. Storage at an elevated temperature to maintain relatively low viscosity and prevent crystallization.
2. The viscous liquid must be pumped such that is mixes with the effluent.
3. The mixing must be sufficient enough to fully dissolve the syrup in the effluent.

1.5.3. Brewery Waste

The waste effluent of breweries is mainly composed of ethanol and sucrose in various concentrations and dilutions. These two constituents have different properties as a carbon source.

Ethanol (C_2H_6O) is a highly flammable, clear liquid most often used as an additive to motor fuel. Many alcoholic beverages contain ethanol. Denatured ethanol can be purchased for $8.93 per liter and must be stored in flammable liquid storage areas away from oxidizers, high temperatures, and flames. The boiling point of ethanol is 78.5 degrees Celsius, the freezing point is -115 degrees Celsius, and its pH is approximately 7.[29] Ethanol is often used in denitrification and is known to have a high denitrification rate of 9.6 mg NO3-N/ (g VSS-h), along with a low sludge yield of 0.42 m MLSS/ g COD.[30]

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[26] Corn Naturally. (n.d.). HFCS COMPOSITION. Retrieved February 04, 2016, from http://www.cornnaturally.com/hfcs-scientific-data/HFCS-Nutritional-Equivalencies/Composition

[27] deBarbadillo, C. et. al.,(2008). Got Carbon? Widespread biological nutrient removal is increasing the demand for supplemental sources. Water Environment Federation http://www.webpages.uidaho.edu/ce432/WET-Got%20Carbon.pdf

[28] Pretorius, C., Kilian, R., & Jannone, J. (2006). *GIVE YOUR DENITRIFICATION BUGS A SUGAR HIGH* [Scholarly project]. In *Water Environment Foundation*. Retrieved February 3, 2016.

[29] Nutrients Review. (2015). Alcohol (Ethanol) Chemical and Physical Properties. Retrieved February 04, 2016, from http://www.nutrientsreview.com/alcohol/definition-physical-chemical-properties.html

[30] Ma, Y. Peng, Y. Wang S. (2007). Denitrification potential enhancement by addition of external carbon sources in a pre-denitrification process. Journal of Environmental Sciences 19(2007) 284-289. Retrieved October 2, 2015.

Sucrose ($C_{12}H_{22}O_{11}$), also known as sugar, is a molecule comprised of glucose and fructose. Sucrose is found in waste effluents from industrial beverage manufacturing, breweries and sugar production facilities. Sucrose has a melting point of 185.5 degrees Celsius and a neutral pH.[31] The TCOD of sucrose is 1.1 g O_2/ g sucrose.[32]

A study completed by the Italian Association of Chemical Engineering (IACE) tested sucrose as an external carbon source for denitrification of wastewater from explosive and ammunition industries, whose wastewater generally contains high nitrate concentrations. With an appropriate set up, the IACE discovered that sucrose could achieve high denitrification rates in the wastewater. However, two reactors in series had to be set up to achieve a pH that did not cause inhibiting effects of nitrites, and this was not the case with methanol or acetic acid. Furthermore, complete nitrate removal was only found with methanol in their study.[33]

Sucrose is combustible and finely dispersed particles can form explosive mixtures in air, but is not considered flammable in solid state. If sucrose comes in contact with strong oxidants, there may be a reaction, creating a fire hazard. Sucrose may cause skin, eye, and lung irritation, but is not a known human carcinogen.[34]

1.5.4. Dairy Waste

Dairy products include milk, yogurt, cheese, and more. Their production creates wastes and byproducts in the process. Dairy byproducts have potential to be effective carbon sources with the main components found in the waste being lactose and lactate.[35]

Lactose is a waste product generated through the production of dairy products. Lactose's chemical formula is $C_{12}H_{22}O_{11}$, similar to the structure and formula of sugar.[36] This compound is non-flammable, but emits toxic fumes under fire conditions. Lactose is not a carcinogen and does not have any known chronic effects. Protection is necessary when handling lactose in case of irritation to skin and eyes. Lactose should be stored in ambient temperature and a tightly closed container to ensure an unlimited shelf life.[37] In dairy waste, 1.00 kg of lactose produces 1.13 kg of COD, but COD can vary in dairy waste depending on the concentration of contents. Lactose's

[31] PubChem. (2004, September 16). Sucrose. Retrieved February 04, 2016, from http://pubchem.ncbi.nlm.nih.gov/compound/sucrose
[32] Langeland, W. E., & Filipiak, D. J. (2016, February 4). *Food Processing Wastewater Treatment Design*. Lecture.
[33] De Filippis, P., Di Palma, L., Scarsella, M., & Verdone, N. (2013). Biological Denitrification of High-Nitrate Wastewaters: A Comparison Between Three Electron Donors. *Chemical Engineering Transactions, 32*, 319-324. Retrieved February 4, 2016, from http://www.aidic.it/cet/13/32/054.pdf
[34] "Sucrose." *PubChem OPEN CHEMISTRY DATABASE*. National Center for Biotechnology Information, 30 Jan. 2016. Web. 04 Feb. 2016.
[35] Znanstveni, Izvorni Rad. "The Potential of Dairy Wastewater for Denitrification." *Faculty of Food Technology and Biotechnology, University of Zagreb* (n.d.): n. pag. Web. 8 Feb. 2016.
[36] Bursey, Robert G. "New Industrial Uses of Dairy Products." *National Agricultural Library*. United States Department of Agriculture.
[37] "MSDS Lactose." *Hummelcroton.com*. Hummel Croton. Web. 04 Feb. 2016.

melting point is 203.5°C. The price of lactose is $3.99 per pound and the pH of lactose is mostly neutral, but can range from 6-10.[38]

Lactate is another byproduct of dairy product production. Lactate, or the chemical name lactic acid ($C_3H_6O_3$), is very dangerous and can burn the eyes, skin, and digestive and respiratory tracts. Lactate is also dangerous in proximity to fire, moisture, or water.[39] The boiling point of lactate is 200°C and the melting point is 17°C.[40] Lactate is acidic, with a pH of 2.4 and a COD of 1.07 mg COD per mg of lactic acid. The price of lactic acid is $2.98 for a 5-ounce of an 88% solution.[41]

Dairy wastewater has been proven to be an alternative carbon source for the denitrification process with concentrations of lactose, lactate, or both. During one experiment, a maximum nitrate reduction rate was 5.75 mg NO_3-N/Lh. The concentrations of lactose and lactate were unknown during the experiment because the compositions in the wastewater vary from day to day.[42]

1.5.5. Winery and Alcoholic Beverages Waste

Wine and alcohol production creates a waste stream that is mainly composed of ethanol in various concentrations of water. Ethanol as a carbon source was previously discussed in section 1.5.3 concerning waste of breweries.

1.5.6. Biodiesel Production Waste

As described in earlier sections, glycerol is the main byproduct of biodiesel production. Glycerol ($C_3H_8O_3$) is a sugar alcohol compound most commonly found in pharmaceutical products. The cost of pure glycerol is approximately $7.50 per liter. Glycerol must be stored in a sealed container in a cool environment, although the chemical is not explosive. Experiments have been run involving glycerol in denitrification of wastewater. Results have shown that glycerol is successful in the denitrification process. During one experiment, sludge concentration had to be regulated because there was an overproduction of biomass. However, this ended up being desirable because the relationship between the amount of biomass and nitrogen removal is a positive linear trend.[43]

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[38] World Bank Group. "Dairy Industry". Pollution Prevention Control, 1998. Retrieved from <http://www.ifc.org/wps/wcm/connect/2668f38048855c0e8adcda6a6515bb18/dairy_PPAH.pdf?MOD=AJPERES>
[39] Material Safety Data Sheet Lactic Acid." *Trade-chem.com*. Chemtrade International.
[40] "Lactic Acid". Corbion Purac, 2014. Retrieved from <http://www.lactic-acid.com/physical_properties.html>
[41] "The activated sludge system". The Wastewater Handbook, 2013. Retrieved from <http://www.wastewaterhandbook.com/documents/organic_material_metabolism/211_OMBM_COD.pdf>
[42] Dragicevic, Tibela. "The potential of dairy wastewater for denitrification". University of Zagreb, 2010. Retrieved from <file:///C:/Users/Dallen/Downloads/Mljekarstvo_29_9_2010_191_197%20(1).pdf>
[43] Grabinska-Loniewska, A. Slomczynski T. Kanska Z. Denitrification Studies with Glycerol as a Carbon Source. Institute of Environmental Engineering, Warsaw Technical University. Retrieved October 6, 2015.

Glycerol has a freezing and boiling point of 18 and 290°C respectively. The COD of glycerol has been reported as 1160 mg/g substance and the pH at 7.2.[44]

1.5.7. Sugar Production Waste

Sugar is made through a process that results in wastes with high concentrations of sugars and ethanol. Both of these components' performances as a potential carbon source have been previously discussed in section 1.5.3 brewery waste.

1.5.8. Municipal Solid Waste Landfill Leachate

Methane (CH_4) is a potent greenhouse gas produced by solid waste landfills. Low in cost and common at many wastewater treatment plants, methane is viewed as a valid option to use in denitrification. Only aerobes are able to metabolize methane. Aerobes only survive in aerobic environments, and denitrification must be performed under anoxic conditions. Methane has been experimentally proven to perform denitrification in wastewater. However, denitrification only occurred at 8-13%, or 3.5-4.0 mg/L. Instead methane can be converted into methanol and used as the source of the electron donor.

Methane is known to be a highly flammable material requiring special storage units. Special training would be needed with any employees who are required to handle methane. Safety training would be required of employees in case of methane leaks. The boiling point of methane is -162°C and the freezing point is -182.5°C.[45] COD of methane is 4 g COD/g CH_4.[46] Cost and pH of methane could not be accurately reported.

1.5.9. Chemical Manufacturing Waste

Many industries within chemical manufacturing include production and use of antifreeze, windshield washer fluids, and raw chemicals. Each industry produces a different composition and concentration of waste.

The production of windshield washer fluid is one chemical manufacturing source that leads to a waste product of diluted methanol. Methanol (CH_3OH) is an alcohol that acts as an effective electron donor and is commonly used in wastewater denitrification. UBWPAD employees have specifically declared that they do not want to use methanol at their facilities because of safety concerns. Storing methanol onsite requires a local firefighter to constantly be in contact with UBWPAD employees. Methanol requires special storage units and areas because of its flammability. Safety training on handling and emergency procedures would be required for all

[44] Robertson, Steve. "Glycerol." *Inchem.org*. National Centre for Ecotoxicology & Hazardous Substances, Mar. 2002. Web.
[45] Boyle, Richard, and Peter Witherington. "Guidance on Evaluation of Development Proposals on Sites Where Methane and Carbon Dioxide Are Present." *Nhbc.co.uk*. National House-Building Council, Mar. 2007. Web.
[46] "Anaerobic Digestion." *Waste Water Handbook*. Web.

employees, which could be very expensive.[47] Methanol is priced at $1.13 per gallon.[48] The freezing point of methanol is -97.8°C and the boiling point is 64.5°C. Methanol does not have a specific pH because pH is associated with water solutions. Methanol contains 4.00mg COD/mg TOC.[49]

Another chemical produced as a waste product by some chemical manufacturers is isopropyl alcohol (IPA) with the IUPAC name 2-propanol and the chemical formula $CH_3CHOHCH_3$. This is an organic compound which can be used in aiding the denitrification process.[50] According to the MSDS, some precautions should be taken when working with this highly flammable compound. IPA is a skin and eye irritant and should not be ingested or inhaled. IPA is also highly flammable and potentially explosive and must be contained in a separate area, where ventilation is available. The freezing point of IPA is -88.5°C and the boiling point is 82.5°C. The pH of IPA is not available because pH is associated with water solutions.[51] The COD of this compound is 2.23 grams of oxygen per gram of chemical.[52] One gallon of 99.5% IPA is $25.00/gallon from ULINE, but can be found cheaper on eBay. Sources were not found on the performance of IPA in denitrification of wastewater.

Acetone is a chemical that can be found in manufacturing wastes and may be utilized for denitrification of wastewater.[53] The chemical should not come in contact with eyes or skin and should not be ingested or inhaled. Acetone is flammable in the presence of open flames and can be explosive and must be stored in cooled containers in a separate and well-ventilated area. The area where acetone is worked with must be well ventilated. Acetone's freezing point is -95.35°C and the boiling point is 56.2°C.[54] The pH and use within denitrification is not available for acetone. The COD of acetone is 1.92g COD/g acetone.[55] Sigma Aldrich sells acetone for $495.00 for 4×4L.

An additional waste product of chemical manufacturers is acetate which is a commonly used alternative carbon source for denitrification.[56] In some cases, acetate has been found to be a

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[47] Mark Johnson. Personal Correspondence. 2015.
[48] Ridge, Tom, and Mary E. Peters. "The Methanol Alternative to Gasoline." *The New York Times*. The New York Times, 23 Feb. 2012. Web. 08 Feb. 2016.
[49] "The activated sludge system". The Wastewater Handbook, 2013. Retrieved from <http://www.wastewaterhandbook.com/documents/organic_material_metabolism/211_OMBM_COD.pdf>
[50] "Wastewater Treatment Fact Sheet: External Carbon Sources for Nitrogen Removal." United States Environmental Protection Agency, 1 Aug. 2013
[51] "Isopropyl Alcohol MSDS." Sciencelab.com, Inc.
[52] Bridie´, A., Wolff, C., & Winter, M. (1979). BOD and COD of some petrochemicals. *Water Research, 13*(7), 627-630.
[53] Gu, A., & Onnis-Hayden, A. (2010). PROTOCOL TO EVALUATE ALTERNATIVE EXTERNAL CARBON SOURCES FOR DENITRIFICATION AT FULL-SCALE WASTEWATER TREATMENT PLANTS. *Water Environment Research Foundation*. Retrieved August 31, 2015.
[54] *Acetone MSDS*. Sciencelab.com.
[55] Bridie´, A., Wolff, C., & Winter, M. (1979). BOD and COD of some petrochemicals. *Water Research, 13*(7), 627-630.
[56] *Wastewater Treatment Fact Sheet: External Carbon Sources for Nitrogen Removal*. (2013). USEPA.

more effective source of denitrification when compared to methanol and ethanol, two other common alternative carbon sources.[57] Acetate is the ion derived from acetic acid.[58] Acetic acid is also commonly used an alternative carbon source for denitrification.[59] Dilute solutions must be used to prevent flammability and specialty storage is needed to prevent freezing. The freezing point of acetate is 17°C and a boiling point of 118°C. The pH of acetate is 2.4.[60] The COD and cost was not found.

One form of antifreeze is used for de-icing air crafts and airports and is mainly composed of propylene glycol ($CH_3CHOHCH_2OH$). Propylene glycol is a readily biodegradable organic compound. Solutions of both ethylene glycol and propylene glycol have been studied for potential use as an alternative carbon source for denitrification. Waste run off from airport deicing is rich in organics with a 4.7-10gCOD/gNO_3N ratio. Studies demonstrate deicing waste is an effective denitrification source that can be more beneficial than methanol.[61] Propylene glycol has a low risk in handling and storage. According to the MSDS for this chemical, it only has a flammability rating of one, making it a fairly safe chemical to handle. The freezing point of propylene glycol is -59°C and the boiling point is 188°C. The pH is not available for propylene glycol.[62] The COD is reported to be 1.63g COD/g propylene glycol.[63] Propylene glycol is $16.49 per gallon at Sears, but industrial quotes may vary.

Chemical manufacturers sometimes produce glycerin as a byproduct. Micro-C, UBWPAD's current carbon source, is mainly composed of glycerin as mentioned previously. Glycerin can expected to be a potentially effective source as Micro-C. Glycerin is also known as 1,2,3-Propanetriol with the chemical formula $C_3H_5(OH)_3$. The hazards of working with glycerin are low with little to no risk of physical contact or inflammation. The boiling point of glycerin is 290°C and the melting point is 19°C.[64] An approximate price for this chemical is $1.34/lb.[65] The COD for glycerin could not be determined.

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[57] Cormier, M., Suchecki Jr., R., Pertuit, R., Brown, D., & Cormier, T. (2010). *Compound for denitrifying wastewater*. United States Patent and Trademark Office.
[58] Acetate. (2015, October 1). Retrieved November 6, 2015, from http://pubchem.ncbi.nlm.nih.gov/compound/acetate#section=Related-Compounds-with-Annotatiohttp://pubchem.ncbi.nlm.nih.gov/compound/acetate#section=Related-Compounds-with-Annotationn
[59] ScienceLab. (2013). *Acetic acid MSDS*. Sciencelab.com.
[60] deBarbadillo, C. et. al.,(2008). Got Carbon? Widespread biological nutrient removal is increasing the demand for supplemental sources. Water Environment Federation http://www.webpages.uidaho.edu/ce432/WET-Got%20Carbon.pdf
[61] Liang, W. (2013). *Evaluation of an Industrial By-product Glycol Mixture as a Carbon Source for Denitrification*. Blacksburg, Virginia: Virginia Polytechnic Institute.
[62] ScienceLab. (2013). *Propylene Glycol MSDS*. Sciencelab.com.
[63] Bridie´, A., Wolff, C., & Winter, M. (1979). BOD and COD of some petrochemicals. *Water Research, 13*(7), 627-630.
[64] ScienceLab. (2013). *Glycerin MSDS*. Sciencelab.com.
[65] "Glycerin." *Bulk Apothecary*. Web. 06 Apr. 2016.

1.6. Experimental Background

Various tests were performed on the wastewater samples in order to evaluate the potential of the various carbon sources for denitrification at the plant. The tests performed determined the values of COD, and nitrate content, and evaluated reaction kinetics. COD is "a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite." In wastewater applications, COD and BOD are commonly used to indirectly measure organic content. It is important for organic content in wastewater to be low as it leaves the treatment plant, thus BOD and COD levels are monitored to ensure this happens. However, only COD tests were performed for this project. COD tests can be completed in a couple of hours while BOD tests take several days. As stated previously in the background chapter, it is important to keep nitrogen levels low as high nitrogen concentrations can lead to several deleterious effects. Therefore, tests were run to determine the nitrate concentration in the wastewater. Lastly, studying the kinetics within a reactor assisted in the design of the process flow and reaction rates to deduce if a higher flow rate or more contact time is needed. Methods for these experiments are further described in the second chapter.

1.6.1. COD Testing

COD is a measure of the organic content in wastewater. Typically, COD tests are used to test wastewater or contaminated natural waters. The tests are standard; a sample is taken, transferred to a test vial with the necessary reactants, and put into an incubator for 2 hours at 150°C. Chemicals found in wastewater include various organics and inorganics; therefore, potassium dichromate is ordinarily used in combination with sulfuric acid to create a strong oxidizing environment.[66]

1.6.2. Nitrate Testing

According to the United States Environmental Protection Agency (USEPA), nitrates are a form of nitrogen found in land and water environments. They are necessary nutrients for plants, but in excess, they can be harmful to water ecosystems and can decrease water quality. An increase of nitrates in water causes low levels of dissolved oxygen (DO). Low levels of oxygen in the water create a toxic environment to aquatic lifeforms. To gain perspective, the amount of nitrates, such as ammonia (NH_3) and nitrate (NO_3), in the effluent are typically less than 1 mg/L

[66] Net Industries. (2015). *Chemical Oxygen Demand*. Retrieved from Net Industries: http://science.jrank.org/pages/1388/Chemical-Oxygen-Demand.html

while the influent in wastewater treatment plants can reach up to 30 mg/L.[67] Testing for nitrates can be done with a cadmium reduction method or a nitrate electrode method.

The cadmium reduction method is a colorimetric method. Cadmium in particulate form are mixed with the nitrate, creating nitrites. If the concentrations of nitrite are greater than 1 mg/L, then a color wheel should be used to select the concentrations; otherwise, a spectrophotometer should be used. Since part of the test is subjective, results may vary from lab to lab.[68]

The nitrate electrode method is another common test to measure the amount of nitrates in the water. The nitrate concentration is tested with a probe measuring the amount of nitrate activity in the water. The probe measures the nitrate concentration by transferring the electric signal from the probe to a scale read in millivolts. Readings can be affected by high concentrations of chloride or bicarbonate ions in the sample and by changes in temperature.[69]

1.6.3. Reactor Kinetics

In industry, bench scale reactors are utilized to collect kinetics data before developing a large-scale process. They are used to examine various ranges of pressures, temperatures, and ratios of reactants or catalysts. The rates of the various reactions are dependent upon the kinetic processes, physical, chemical, and biological. Chemical kinetic processes refer to the interaction between molecules, whereas the physical kinetic processes refer to mixing and changing the pressure or the temperature of a system. A basis for comparison is typically selected when designing an experiment. Comparisons between results of the bench scale reactor experiments can be compared to typical reactions.[70]

In order to complete this experiment, the amount of alternative carbon source to add to the batch reactor had to be determined. Several factors impact the amount of sample added to the system including COD, substrate to biomass ratio (F/M), and mixed liquor volatile suspended solids (MLVSS). COD has been previously discussed and explained prior. The F/M represents the food, carbon substrate, to microorganism ratio.[71] MLVSS are the volatile suspended solids that are present in the wastewater being treated. In order to find the MLVSS, first the mixed

[67] Environmental Protection Agency. (2012, March 6). *Water: Monitoring and Assessment: 5.7 Nitrates*. Retrieved from EPA: United States Environmental Protection Agency: http://water.epa.gov/type/rsl/monitoring/vms57.cfm
[68] Environmental Protection Agency. (2012, March 6). *Water: Monitoring and Assessment: 5.7 Nitrates*. Retrieved from EPA: United States Environmental Protection Agency: https://www.epa.gov/sites/production/files/2015-06/documents/stream.pdf
[69] Ibid.
[70] Snyder, J. R., Hagerty, P. F., & Molstad, M. C. (1957, April). *Operation and Performance of Bench Scale Reactors.* Retrieved from ACS Publications: http://pubs.acs.org/doi/pdf/10.1021/ie50568a033
[71] Gu, A. and Hayden, A. (2010). Protocol to Evaluate Alternative External Carbon Sources for Denitrification at Full-Scale Wastewater Treatment Plants. WERF.

liquor suspended solids (MLSS) must be found.[72] The two are interrelated and the procedure for finding them is described in the sections below.

[72] "Mixed Liquor Volatile Suspended Solids (MLVSS) & (MLSS) - EBS - Wastewater Training and Consulting." *EBS Wastewater Training and Consulting RSS*. Wastewater Training and Consulting, 2016. Web. 21 Apr. 2016. <https://www.ebsbiowizard.com/2011/01/mixed-liquor-volatile-suspended-solids-mlvss-mlss/>.

2. Methods

The research performed prior to testing identified various organics chemicals that have potential as a carbon source for denitrifying wastewater. Availability was next assessed by finding local industries with ready waste streams of the alternative carbon sources. The wastes with the companies producing them are displayed in Table 2**Error! Reference source not found.**. These companies were all contacted and those that were able to provide waste samples for testing are marked as obtained. For industries that samples were not able to be obtained from, similar samples were developed in the lab and are marked as developed. UBWPAD currently uses Micro-C for the carbon source in denitrification. A sample of Micro-C was obtained from UBWPAD to develop a baseline of treatment effectiveness. Biodiesel production waste was obtained from another Major Qualifying Project at WPI with Professor Clark.

Table 2: Establishing Alternative Carbon Sources

Industry Waste Type	Composition	Company Contacted	Obtained/Developed
Chemical waste	Glycerin; water	DOW Chemical, Marlborough, MA	Obtained
Windshield wiper waste	Methanol; water	Elite Chemical, Springfield, MA	Obtained
Dairy waste	Lactose; lactate; water	Garelick Farms, Lynn, MA	Obtained
Beverage waste	Corn syrup; water	Polar Beverages, Worcester, MA	Developed
Sugar production	Sugar; water	N/A	Developed
Airport deicer	Ethylene glycol; water	Worcester Airport, Worcester, MA	Developed
Biodiesel byproduct	Glycerol; potassium hydroxide; canola oil; methanol	Professor Clark, WPI	Obtained
Micro C	Glycerin	UBWPAD	Obtained

A new sample of wastewater was obtained each week from the UBWPAD to perform COD testing, nitrate testing, and kinetic reactor testing with the different carbon sources. The following sections discuss the procedures in detail.

2.1. COD Testing

All COD tests were done using Bioscience, Inc. 20-900 mg/L COD vials. The procedure for creating a COD standard curve and analyzing samples was taken from MQP advisor Professor

Bergendahl, the 19th edition of the "Standard Methods for the Examination of Water and Wastewater", and the Bioscience, Inc. COD methods.

2.1.1. COD Calibration Curve Procedure

Three different dilutions of potassium hydrogen phthalate (KHP) and distilled water were created and then 2.5 mL of each solution were added to the COD vials. The dilutions created were 170 mg/L, 425 mg/L and 680 mg/L. Next, the vials were shaken to mix the solution, and each vial was heated for two hours at 150°C to allow for digestion. After heating, the samples were removed from the incubator, agitated and then allowed to settle for ten minutes. This step is required to avoid diffraction with the light beam. Following settling, the samples were transferred to the spectrophotometer cuvettes, and readings were taken at a wavelength of 600 nm after zeroing to a blank.

A plot was made with COD values of the standards on the x-axis and absorbance of the dilutions on the y-axis. A line of best fit was found and the slope of this line was found to be 0.0004. COD values of the other samples were found using Equation 4.

Equation 4: COD Calculation from Absorbance

$$COD\ Sample\ \left[\frac{mg}{L}\right] = 1 + absorbance[nm] \times 0.0004$$

2.1.2. COD Procedure

Samples to be tested were diluted as needed and 2.5 mL of the sample added to the COD vial. Next, the vials were shaken to mix the solution, and each vial was heated for two hours at 150°C to allow for digestion. After heating, the samples were removed from the incubator, agitated and then allowed to settle for ten minutes. This step is required to avoid diffraction with the light beam. A spectrophotometer was used to analyze each sample through SimpleReads software program shown in Figure 3. Following settling, the samples were transferred to the spectrophotometer cuvettes, and readings were taken at a wavelength of 600 nm after zeroing to a blank. The COD standard curve was used to convert the readings from absorbance to mg/L COD.

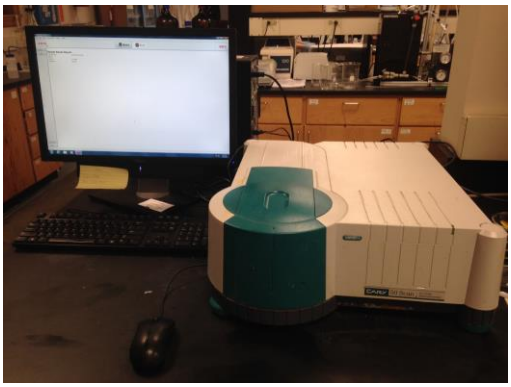


Figure 3: COD Spectrophotometer and SimpleReads Computer Software

2.2. Nitrate Testing

To complete the nitrate testing, the electrode operation was tested first. This procedure measured the slope of the electrode, which in return checked the electrode operation. The slope was measured as the change in millivolts (mV) over the change in concentration. Once the nitrate electrode was properly set up and running, the electrode was connected to a meter and set to millivolts (mV) mode, shown in Figure 4. The standard procedure for low level calibration was used as some denitrification produced nitrate concentrations below 1.4 ppm. To begin this method the procedure calls for 100 mL of distilled water and 1 mL ionic strength adjuster Cat. No. 930711 (ISA). However, ISA was not provided and was substituted with nitrate interference suppressor solution (NISS) Cat. No 930710 for this procedure and all future procedures needing ISA. When testing samples a ratio of 1:1 is needed between sample and NISS. For the standard curve there is 10.1 mL of NISS required for every 90.9 mL distilled water. In a 200 mL beaker 100 mL of distilled water was mixed with 11.1 mL NISS. 100 ppm nitrate standard was used for the procedure. The following Table 3 displays the amount of 100 ppm nitrate standard added to the distilled water and NISS mixture and the nitrate concentrations of the resulting solutions.

Table 3: Values Used to Develop the Nitrate Standard Curve

Volume Nitrate Standard Added (mL)	Concentration of N (ppm)
0.1	0.1
0.1	0.2
0.2	0.4
0.2	0.6
0.4	1.0
2.0	2.9
2.0	4.7

The concentration of nitrate and the corresponding mV reading from the electrode could then be used to produce a standard curve. This curve could then be used to convert mV readings

into nitrate concentrations. The nitrate electrode readings are sensitive to temperature and so temperature was recorded with every nitrate electrode reading to account for any discrepancies.

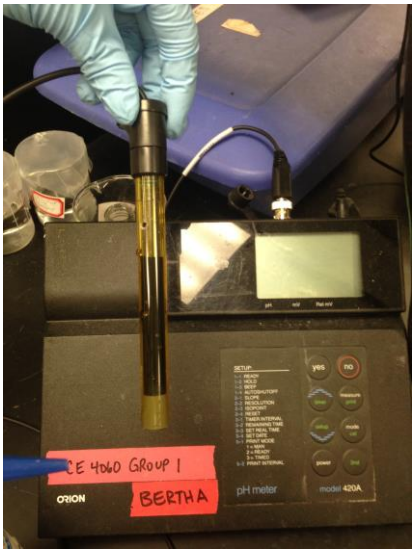


Figure 4: Nitrate Probe and Display

First, regular wastewater was tested to conclude what the normal concentration of nitrate was in wastewater. The amount of nitrate in regular wastewater was then used to compare with other wastewater solutions once a carbon source was added. The carbon source was mixed with the wastewater and then a 20 mL sample was removed and mixed with 20 mL of NISS for one minute. The nitrate probe was then placed into the solution for thirty seconds and the meter reading was recorded and used to determine the concentration of nitrate in the solution using the standard curve. This procedure was used in the reactor kinetic experiment to measure the difference in nitrate concentrations for regular wastewater and wastewater with an added carbon source. The readings were taken and analyzed to conclude which carbon sources caused the concentration of nitrate in wastewater to decrease the most.

2.3. Reactor Kinetics Experiments

The following procedure was modified from "Protocol to Evaluate Alternative External Carbon Sources for Denitrification at Full-Scale Wastewater Treatment Plants" by Gu and Hayden.[73] A nitrate utilization rate experiment was performed using a small batch reactor to analyze the reaction kinetics of the alternative carbon sources. This was achieved by measuring nitrate and COD readings over time to analyze the specific denitrification rate and the COD/N ratio. Nitrate levels were low, less than 1 ppm, due to cold seasonal operation of the wastewater

[73] Gu, A. and Hayden, A. (2010). Protocol to Evaluate Alternative External Carbon Sources for Denitrification at Full-Scale Wastewater Treatment Plants. WERF.

treatment plant, therefore an additional source of nitrate was added to the reactor to ensure nitrate could be observed. Adding additional nitrate produced more dependable results as the lowest limits of the probe would not be reached. Approximately 10 mg of sodium nitrate was added to each reactor at the start of every test. This number was decided upon because research showed that nitrate levels at treatment plants typically begin at about 8 ppm.[74] After measuring the nitrate readings in our wastewater samples a mass balance was calculated and determined that approximately 10 mg of sodium nitrate would be needed to achieve near to an 8 ppm nitrate starting point for each test.

In order to find the best candidates most efficiently, a shorter test was first performed on all potential sources in order to select the top candidates to study closer. Short tests were two hours long with less samples taken, and more extensive tests were four hours with more samples taken. The exact procedures are below.

Before completing any reactor tests, the MLVSS of the wastewater from UBWPAD were measured in order to decide the amount of carbon source to add to the reactor test. This was done by vacuum filtering 50 mL of wastewater through 1.5 µm nominal pore size glass fiber filters that had previously been dried for 24 hours in an 105°C oven and then weighed. The wet filters were left in the oven for 24 hours. Once removed, the filters were weighed to determine the total suspended solids in the wastewater using Equation 5.

Equation 5: MLSS Equation

$$\frac{total\ suspended\ solids[mg]}{[L]} = \frac{(A - B) \times 1{,}000}{C}$$

$$A = weight\ of\ filter + dried\ residue\ [mg]$$

$$B = weight\ of\ filter\ [mg]$$

$$C = sample\ volume\ [mL]$$

The dried filters with residue were then put in a 500 degree Celsius oven for one hour before being removed and weighed. The MLVSS were then calculated using Equation 6.

[74] Leverage, E. (2015). All wastewater foam is not alike. Retrieved from http://www.environmentalleverage.com/All_foam_is_not_alike.htm

Equation 6: MLVSS Volatile Solids Equation

$$\frac{volatile\ solids[mg]}{[L]} = \frac{(A-B)\times 1{,}000}{C}$$

$$A = weight\ of\ residue + filter\ before\ ignition[mg]$$

$$B = weight\ of\ residue\ and\ filter\ after\ ignition\ [mg]$$

$$C = sample\ volume\ [mL]$$

The total suspended solids were tested and recorded for each wastewater sample taken from UBWPAD. It was assumed that a consistent MLSS would yield a consistent MLVSS, resulting in little to no change in MLVSS values throughout testing.[75] Samples of wastewater from the UBWPAD were taken weekly to provide consistently fresh water for testing.

Once the MLVSS had been determined the amount of alternative carbon source to be added to the reactor was calculated using Equation 7.

Equation 7: Determining Amount of Carbon Source to Add to Reactor

$$\frac{F}{M} = \frac{(V_{cs}\times COD)}{V_{ML}\times X}$$

V_{CS}: volume of alternative carbon source added to the test in liters.

COD: the tested Chemical Oxygen Demand of the alternative carbon source in mg/L

V_{ML}: volume of the mixed liquor in the test in liters

X: concentration of mixed liquor volatile suspended solids (MLVSS) in test in mg VSS/L

A substrate to biomass ratio (F/M ratio) must be chosen and experimented with and must not be unrealistically high or ineffectively low. The determination must be made by trial and error but for most situations a value between 0.02 and 0.05 mg COD/mg VSS should lead to desirable results. Therefore, for the reactor tests an F/M ratio of 0.035 mg COD/mg VSS was used for all samples.

A 2 liter Erlenmeyer beaker was used as the batch reactor with 1.6 liters of wastewater added inside. Nitrogen gas from a gas tank was added to the beaker from a tube with a sparger at the end. Enough nitrogen gas was added to stir the wastewater continuously. Parafilm was used to cover the top of the flask with air holes cut into to release pressure. This is the procedure to set up the reactor, the short and long test of each sample are explained below.

[75] "MLVSS/MLSS Ratio." *MLVSS/MLSS Ratio*. Wastewaterinfo.com, n.d. Web. 27 Jan. 2016. <http://waterfacts.net/Treatment/Activated_Sludge/MLVSS-MLSS_Ratio/mlvss-mlss_ratio.html>.

To begin the short test a 2.5 mL sample was taken from the reactor for COD analysis. Additionally, 20 mL was taken for pH and nitrate analysis and temperature was recorded. After this, the calculated amount of carbon source was added to the reactor and allowed to mix for two hours. At the end of the two hours the same tests performed in the beginning were performed at the end.

The long test was set up with the same procedure as the short test. Samples were taken before adding the carbon source and then every 10 minutes for the first hour and every 30 minutes for the following 2 hours. The analysis for the samples was the same as the short test. The desired pH was 7-7.5 as it is for wastewater plants to maintain a nearly neutral pH. At the end of the test, a 50 mL sample was removed from the reactor for MLSS analysis.

The data collected were used to analyze the COD over time and the specific denitrification rate (SDNR) of the carbon source in the wastewater. COD during the final test was plotted versus time to observe the changes more easily. Little to no change in COD was desired, but slight decreases and fluctuations were expected from consumption during denitrification. Large decreases and fluctuations were undesirable to the wastewater treatment process.

To calculate the denitrification rate, a graph of the nitrate concentration versus time was made. The graph can produce up to three slopes: the first and steepest representing consumption of readily biodegradable COD (rbCOD), the second steepest representing consumption of slowly biodegradable COD (sbCOD), and the last and least steep representing the endogenous decay and consumption of nitrate by cells. It was assumed the rbCOD would be the applicable data used for denitrification. The line representing denitrification was determined by taking the linear line of best fit of the initial decrease in nitrate concentration until the nitrate concentration stabilized or began to rise again. Taking the slope of the initial decrease allowed a linear relationship to be applied to the SDNR equation. Equation 8 is used to calculate the SDNR. The value of 1,440 accounts for converting minutes to days. MLVSS was calculated by taking the MLSS of the wastewater sample and the MLSS at the end of the final reactor test and averaging the two. The averaged value was then multiplied by 0.8 to estimate the respective MLVSS.[76] The more negative the value of SDNR, the more rapidly denitrification occurred with the carbon source used.

[76] Gu, A. and Hayden, A. (2010). Protocol to Evaluate Alternative External Carbon Sources for Denitrification at Full-Scale Wastewater Treatment Plants. WERF.

Equation 8: SDNR Equation

$$SDNR = 1{,}440 \times \frac{\frac{dN1}{dt}}{X}$$

SDNR= the specific denitrification rate [kgN/kgVSS/d]

dN1/dt= the first slope of the nitrate versus time graph [mg N/L*min]

X= MLVSS concentration during reactor test [mg/L]

3.0. Results and Discussion

The results from the preliminary and final tests are discussed for each carbon source. For the preliminary tests, the change in pH, COD, and nitrate concentrations from the beginning and conclusion of the tests were analyzed. The results from Micro-C preliminary test were used as a standard to compare with other carbon sources. Carbon sources were selected to undergo final testing based on their results from the preliminary test. For final testing, multiple samples of COD, pH, and nitrate concentration were taken throughout the test. With the results of the test, the SDNR was calculated for each carbon source, based on the data received from the MLVSS test for each wastewater sample. Sample calculations and raw data for these calculations are located in Appendix A and B, respectively.

During the preliminary testing of methanol, ethylene glycol, and glycerin, some foaming occurred in the wastewater. The foam was caused by a low F/M ratio in the aeration basin at UBWPAD due to insufficient sludge wasting, resulting in excess solids in the tank.[77] UBWPAD said that this may be caused by an increase of RAS in the wastewater. Foam in the wastewater could possibly cause error in our testing if foam was in our COD, pH, or nitrate samples. If foam was present in the wastewater, we would carefully take samples out of the batch reactor and make sure that there was no foam present.

3.1. Results of Procedure Development

All reactor tests were originally run in a 2-liter Erlenmeyer flask, on a mixer with a stir bar, and a nitrogen gas sparger turned on until the wastewater was lightly bubbling. Our results gave us an increase of nitrogen in some cases where the carbon sources added did not contain any known compounds that may form nitrates. Based on our initial results, we hypothesized the kinetic reactor may not be anoxic. To enhance nitrogen removal performance, we changed the procedure. The new procedure consisted of removing the stir bar and utilizing the nitrogen sparger to mix the wastewater without developing foam. We covered the reactor with Parafilm to ensure oxygen was not entering the system. The Parafilm had holes, allowing nitrogen gas to leave and not build up pressure within the system.

[77] Leverage, E. (2015). All wastewater foam is not alike. Retrieved from http://www.environmentalleverage.com/All_foam_is_not_alike.htm

The nitrate levels measured within the reactor were still low. We believe the nitrate levels were low because the tests were performed in winter and there is little to no fertilizer runoff entering the plant and bacteria are not as active in colder weather. We used deionized water with the sodium nitrate to find a standard amount to add to the wastewater before testing. Our goal was to create wastewater samples with nitrate concentrations between 5-8 ppm. We were unable to achieve our goal every test because of the variability in the wastewater samples. The final process consisted of using a nitrate level between 3-6 ppm. The amount of nitrate to add was difficult to measure accurately and we lost some samples from sharp increases in nitrate concentration exceeding 8 ppm. The results of the new tests were performed and the data collected was analyzed in the following sections.

3.2. MLVSS (MLSS) Tests

Mixed liquor suspended solid (MLSS) tests were performed on every sample of wastewater and mixed liquor volatile suspended solids (MLVSS) tests were performed once. We assumed MLVSS and MLSS would remain proportional by a ratio of 0.80 as proved accurate by the test we performed. The MLSS averaged 2100 mg/L throughout the preliminary tests performed. The average MLVSS was 1700 mg/L and this value determined the amount of carbon source to add throughout preliminary testing. MLSS of all wastewater samples was measured to ensure there was no significant change to this average and for calculations from final tests. MLSS was measured at the end of final tests. The average of the final MLSS and the MLSS of the wastewater sample was multiplied by 0.80 for the approximate MLVSS to determine the specific denitrification rate.

3.3. Results of Preliminary Tests

A COD test was completed for each carbon source. The preliminary COD test results were utilized to determine the amount of waste sample needed in the kinetic reactor test. Table 4 displays the average COD for each waste sample. The starting and ending nitrate values for each carbon source were also measured in the preliminary tests, and the percent decreases of nitrate are also shown in Table 4.

Table 4: Average COD of Waste Samples and Preliminary Reactor Percent Decrease Nitrate

Waste	Average COD [mg/L]	Percent Decrease Nitrate
Micro-C 2000A	840,000	80.6%
Dairy: Garelick Farms Sample 1	6,420	N/A
Dairy: Garelick Farms Sample 2	7,332	N/A
Chemical Manufacturing: Elite Chemical Windshield Wiper Fluid	1,032	52.0%
Biodiesel Production	16,590,000	83.1%
Airport Deicer: Ethylene Glycol	15,200	43.4%
Chemical Manufacturing: Dow Chemical	75,730	79.8%
Sugar Production: Sugar	1,206,000	86.2%
Beverage Industry: Corn Syrup	830,000	79.8%

Carbon sources with higher COD values required additions of smaller volume to achieve satisfactory denitrification rates. Since the largest percent decrease of nitrate levels are desired, the carbon sources with at least a 70% decrease of nitrate in preliminary tests were considered further for final testing. The carbon sources that did not perform well in the preliminary tests could be tested further by adding larger quantities of the carbon source. However, this could have design constraints because of the large volume of carbon source required and other possible negative impacts on the wastewater. Ten or more milligrams of sodium nitrate were added to the preliminary tests to increase the concentration of nitrate in the water, allowing for more accurate readings from the nitrate probe. Foaming did occur in the preliminary tests, as well as at UBWPAD at the time of sampling. Foaming within the reactor occurred from "insufficient sludge wasting" or under loading within the aeration tank.[78] The foam from the reactor can be seen in Figure 5.

[78] Leverage, E. (2015). All wastewater foam is not alike. Retrieved from http://www.environmentalleverage.com/All_foam_is_not_alike.htm

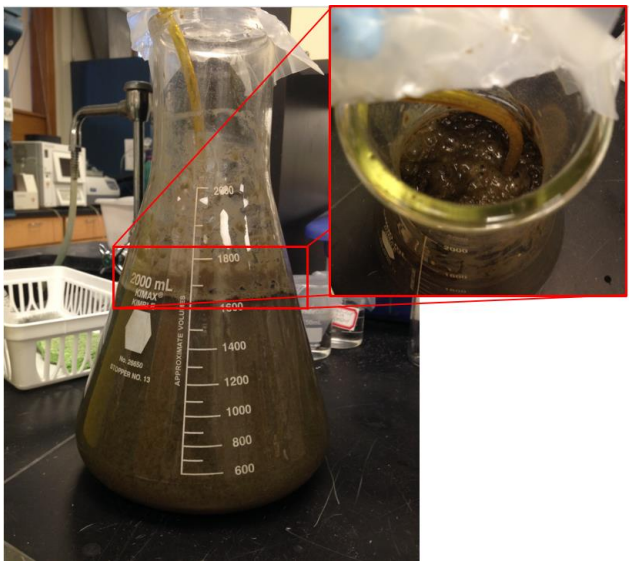


Figure 5: Kinetic Reactor Foam

After initial testing, five carbon sources were selected for further testing: glycerin, biodiesel waste, sugar, corn syrup and Micro-C. Ten nitrate and COD values were taken during the duration of the longer reactor experiment. When the nitrate concentration was measured, the temperature was also recorded because nitrate concentration is temperature dependent. The pH and reactor temperature of the wastewater were recorded at the beginning and then every hour of the experiment. Specific results from the preliminary and long reactor tests are shown in the sections below.

3.2.1. Micro-C

This past year, UBWPAD used Micro-C 2000A in their aeration tanks to denitrify the wastewater. We performed the two hour kinetic reactor test using Micro-C as a baseline to compare alternative carbon sources. Figure 6 displays the Micro-C 2000A solution.

Figure 6: Micro-C 2000A Sample

The Micro-C had a high viscosity and was difficult to transfer from the sample bottle to the beaker to mix in a solution for the COD preliminary test. Micro-C typically has a COD

greater than 1,000,000 mg/L according to standards from the EOS. The spectrophotometer could not read COD values this high and we had to dilute the Micro-C. The COD was recorded multiple times and would not reach 1,000,000 mg/L. We determined the dilution necessary to read the COD for Micro-C called for an amount of chemical that could not be well-mixed. Because the solution could not be completely mixed, the calculation to determine the COD from the dilution was not accurate. The COD of the diluted Micro-C was 840,000 mg/L; this value was used for further calculations.

The COD of the wastewater prior to the preliminary test was 2,650 mg/L with a pH of 6.97. A total of 10.3 mg of sodium nitrate was added to the wastewater to obtain a nitrate concentration of 4.3 ppm. Once this information was measured, 120 µL of Micro-C were added to the batch reactor. At the conclusion of the test, the COD and pH of the wastewater was 2,845 mg/L and 7.31, respectively. The concentration of nitrate was 0.84 ppm. The addition of Micro-C resulted in an 80.7% decrease of nitrate during the preliminary test.

Micro-C was chosen as one of the carbon sources to be tested in the final test as a standard to compare to the other carbon sources. Micro-C was known to be an effective source for denitrification. The data received from Micro-C's final test could be compared with the other carbon sources to identify which sources were as effective as or more effective than Micro-C.

3.2.2. Beverage Waste

We were unable to contact a beverage company that produced a carbon-based waste to be tested. During testing, UBWPAD suggested we test the effectiveness of a corn syrup sample because there was a possible source nearby. Since the sample was requested by the sponsor and final testing had already begun, a preliminary test of corn syrup was not needed and only the final test was run. Store bought corn syrup shown in Figure 7 was used.

Figure 7: Corn Syrup Sample

The COD of the corn syrup was measured to be 830,000 mg/L. The corn syrup was highly viscous and was placed on a hot plate with a stir bar to ensure more accurate sampling.

The percent change of nitrate was calculated from the final test using the beginning and two hour nitrate readings. The overall decrease in nitrate concentration was 79.8%.

3.2.3. Brewery Waste

A brewery company was not able to be contacted to provide a sample for this study. No mockup was created for comparison. There are breweries in the area that can be contacted for further trials by UBWPAD if interested in studying the outcome.

3.2.4. Dairy Waste

Garelick Farms' dairy waste was examined through performing the COD test, nitrate test, and the kinetic reactor test. The waste was received and tested twice for COD. We ran out of time to test the first sample acquired and a second sample was picked up a few weeks later. The first waste sample contained a COD of 25,740 mg/L. The second sample received contained at COD of 7,330 mg/L. The second sample chilled in the refrigerator for six days before able to be tested. The operator of the wastewater treatment plant at Garelick Farms stated the dairy waste composition would begin to vary after 48-hours. The general dairy waste is variant depending upon the day and if any cleaning is being performed on certain systems. Dairy waste also has a pungent odor and odor control is a concern for UBWPAD which makes this waste more problematic. We decided to not proceed with further testing of dairy waste because of the variability in the dairy waste samples and odor concerns. The dairy sample collected can be seen in Figure 8 below.

Figure 8: Garelick Farm Waste Sample

3.2.5. Winery and Alcoholic Beverages Waste

A winery or alcoholic beverages manufacturer was not able to be contacted to provide a sample for this study. No mockup was created for comparison. There are wineries and alcoholic beverage manufacturers in the area that can be contacted for further trials by UBWPAD if interested in studying the outcome.

3.2.6. Biodiesel Production Waste

The unrefined biodiesel waste shown in Figure 9 was composed of glycerol with trace potassium hydroxide, canola oil, methanol and biodiesel. We determined the COD of biodiesel waste was 16,590,000 mg/L. The COD of the wastewater prior to adding the carbon source during the preliminary test was 2,466 mg/L and at the conclusion of the test the COD was 2,541 mg/L. The pH began at 6.86 and ended at 7.34.

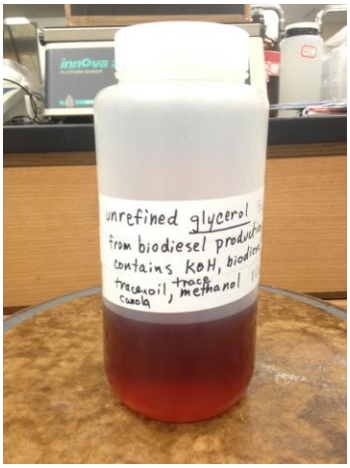


Figure 9: WPI Biodiesel Production Waste Sample

The preliminary reactor experiment resulted in an 83.0% decrease of nitrate concentration, from 3.8 ppm to 0.65 ppm. Since the nitrate reduction was greater than 70.0%, we decided to perform the final test for glycerol.

3.2.7 Sugar Production Waste

A sugar solution was made to measure the COD. The measured COD of pure sugar was 1,206,000 mg/L. Prior to adding sugar, the COD of the wastewater in the preliminary reactor was 2,288 mg/L, and the concentration of nitrate was 4.5 ppm after adding 14 mg of sodium nitrate. A total of 0.13 g of sugar was then added to the preliminary reactor. Throughout the test, the reactor experienced foaming on the surface. After 2 hours, the COD of the preliminary reactor was 2,293 mg/L and the nitrate concentration was 0.62 mg/L, resulting in an 86.2% decrease in nitrate concentration. The pH started at 6.71 and ended at 7.43. Figure 10 displays the sugar sample used for testing.

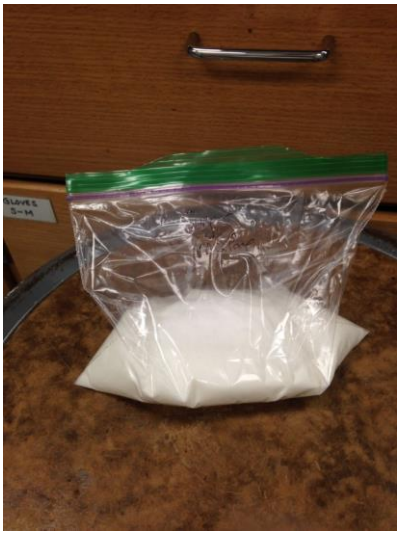


Figure 10: Sugar Sample

Sugar had the highest nitrate removal percentage. We decided to perform the final test to further examine the reaction rates and behaviors of the system.

3.2.8. Municipal Solid Waste Landfill

A carbon source from a municipal solid waste landfill was not found for this study. No mockup was created for comparison. There are landfills in the area that can be contacted for further trials by UBWPAD if interested in studying the outcome.

3.2.9. Chemical Manufacturing Wastes

3.2.9.1. Dow Chemical Waste: (Glycerin)

Waste from DOW Chemical was mailed to WPI and tests were performed. The primary compound found in this waste is glycerin. The COD of the glycerin was measured to be 75,730 mg/L. Figure 11 shows the DOW Chemical sample used for testing.

Figure 11: DOW Chemical Sample

For the preliminary test, the COD of the wastewater prior to adding the glycerin was 1,233 mg/L and the pH was 6.8. The nitrate concentration of the wastewater was 5.2 ppm. A total of 1.3 mL of glycerin was added to the wastewater. At the conclusion of the preliminary test, the COD of the wastewater was 1,126 mg/L and the pH was 7.61. The nitrate concentration was 1.0 ppm, resulting in a 79.8% decrease in nitrate concentration. Glycerin successfully denitrified the wastewater more than 70.0%, and therefore was selected to be tested again in the final test.

3.2.9.2. Elite Chemical Windshield Wiper Fluid: (Methanol) Waste

Waste from Elite Chemical shown in Figure 12 was given to us from their recycle stream. The waste is mainly composed of methanol, with trace dyes. The COD of the methanol waste was measured to be 1,032 mg/L. For the preliminary test, the COD of the wastewater prior to the experiment was 2,019 mg/L and was 3,096 mg/L at the conclusion of the test. The pH began at 7.07 and ended at 7.70. The nitrate concentration decreased by 52.0% during the preliminary test, from 3.0 ppm to 1.4 ppm.

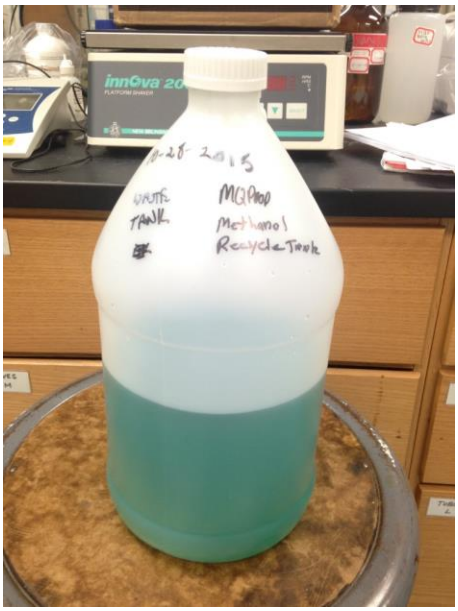


Figure 12: Elite Chemical Windshield Wiper Fluid Sample

The percent of nitrate removal was less than 70%, therefore, we did not perform the final test on the methanol. Since the waste was taken from Elite Chemical's recycle stream, it may not be a consistent or viable option for UBWPAD. The recycle stream is used for the chemical manufacturing of the windshield wiper fluid, thus it may cost UBWPAD money or UBWPAD may not be able to obtain it in sufficient quantities. Elite chemical may not be interested in any business transactions with the materials from their recycle stream because it would add changes to their process dynamics and the recycle stream may be saving them money.

3.2.10. Airport Deicer Waste

We could not obtain deicer fluid runoff from the Worcester Airport due to limited time, mild weather, and lack of direct contact information. Deicer fluid composed of ethylene glycol shown in Figure 13 was obtained from a local store and used as a substitute for the airport waste. The sample was not diluted for the reactor test as it would be if it were an airport waste source.

Figure 13: Deicer Sample

The COD of ethylene glycol was determined to be 15,200 mg/L and 6.3 mL of ethylene glycol were added to the preliminary reactor test. For the preliminary test, the COD of the wastewater prior to adding the ethylene glycol was 1,908 mg/L and was 3,592 mg/L at the end of the test. The pH started at 6.95 and ended at 7.53. The preliminary reactor test of ethylene glycol yielded a 43.4% decrease in nitrate content in the wastewater, from 4.1 ppm to 2.3 ppm. Ethylene glycol was less effective than other potential sources that produced over a 70.0% decrease in nitrate and brought the final nitrate concentration below 2.0 ppm; therefore, deicer fluid was not tested any further.

3.3. Results of Final Tests

Five carbon sources were chosen for final testing for further analysis. They were Micro-C, DOW chemical, biodiesel waste, corn syrup, and sugar solution. Table 5 below summarizes the results.

Table 5: SDNR and Lowest and Highest CODs from Final Tests

Carbon Source	SDNR kgN/kgVSS/d	Lowest COD (mg/L)	Highest COD (mg/L)
Micro-C	-0.053	1,611	2,160
Beverage Production: Corn Syrup	-0.057	968	1,050
Biodiesel Production: Glycerol	-0.103	1,845	2,446
Sugar Production: Sugar	-0.039	983	1,391
Chemical Manufacturing: DOW Chemical (Glycerin)	-0.052	984	1,162

Sugar had the slowest denitrifying rate, followed by glycerin, Micro-C, and corn syrup as seen in the SDNR comparison. Biodiesel waste had the fastest denitrification rate of -0.103 kgN/kgVSS/d. The graphs showing the nitrate concentration over time are presented in the following sections. SDNR was determined using the linear line of best fit of the initial decrease in nitrate concentration until the nitrate concentration stabilized or began to rise again. This linear line represented the consumption of rbCOD for denitrification and allowed a linear interpretation to be applied to the SDNR equation.

Large fluctuations or decreases in COD are undesirable in wastewater treatment. As seen in Table 5, all of the COD ranges do not change more than 650 mg/L. The fluctuation in COD throughout the reaction time would not create any significant issues overall. UBWPAD would need to determine whether or not these variations in COD would affect their system overall. The COD data is presented and discussed more in depth below.

3.3.1. Micro-C

The final three-hour test was performed with Micro-C to compare with the performance of the other carbon sources. Figure 14 shows the nitrate concentrations during the final test of Micro-C.

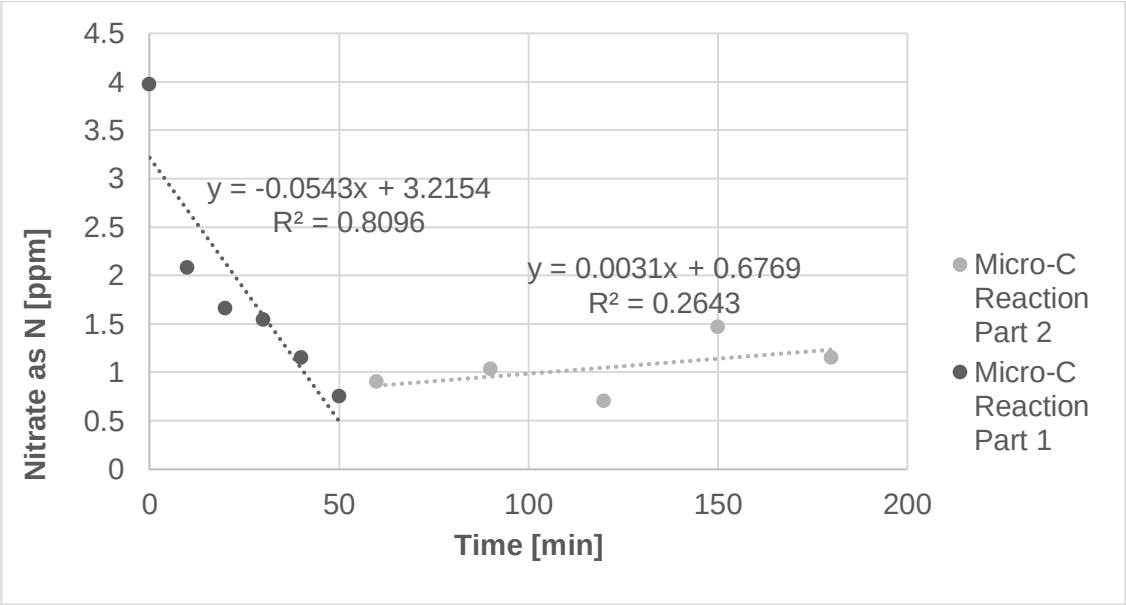


Figure 14: Micro-C Reactor Test Results

The concentration of nitrate starts at 3.97 ppm and the end of the three-hour test the concentration of nitrates decreased to 1.2 ppm. The nitrate concentration is lowest after two hours, where it is 0.70 ppm. The first line depicts the readily biodegradable COD being consumed. The denitrification rate for Micro-C was determined to be –0.053 kgN/kgVSS/d from

the data points on the graph. The COD of the wastewater was also measured throughout the test. Figure 15 shows the COD of the wastewater during the final test for Micro-C.

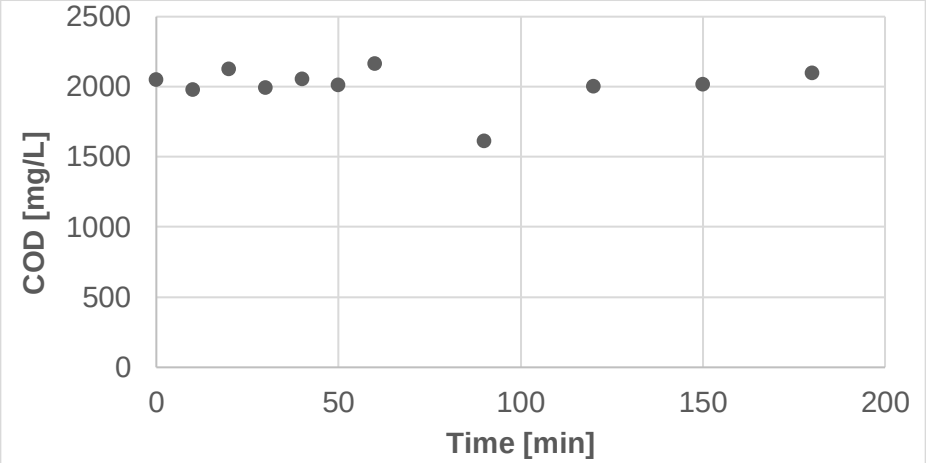


Figure 15: COD over Time for Micro-C

The initial COD of the water was 2,049 mg/L and remained relatively consistent throughout the test. The lowest value was 1,611 mg/L and occurred after 1.5 hours. The highest value was 2,160 mg/L which occurred after 1 hour.

The pH of the water remained neutral for the duration of the test; the pH started at 6.90 and slightly increased to 7.34 at the conclusion of the test. Table 6 shows the hourly reactor temperature and pH of the final Micro-C test.

Table 6: The Hourly Temperature and pH of the Final Micro-C Test

Hour	Reactor Temperature (°C)	pH
0	9.6	6.90
1	15.4	7.20
2	18.5	7.31
3	20.6	7.34

The temperature of the reactor only reached room temperature by the end of the reactor test. We do not believe the reaction caused a significant temperature change because the temperature did not have any sharp increases over the course of the test.

3.3.2. Beverage Production Waste: Corn Syrup

For the final test, 26 mg of sodium nitrate were added to bring the starting nitrate concentration to 4.0 ppm. A total of 120 µL of corn syrup was added to the reactor. The final test yielded a SDNR of –0.057 kgN/kgVSS/d. This value was calculated using the slope from the graph shown in Figure 16. The fastest reaction rate for denitrification mainly occurs in the first half hour as the readily biodegradable COD is consumed. The reaction rate slows down for the

remaining time to consume the slowly biodegradable COD as can be observed in the nitrate versus time graph below in Figure 16. Compared to Micro-C with a reaction rate of –0.053 kgN/kgVSS/d, the corn syrup had a faster reaction rate, but was not significantly different from Micro-C.

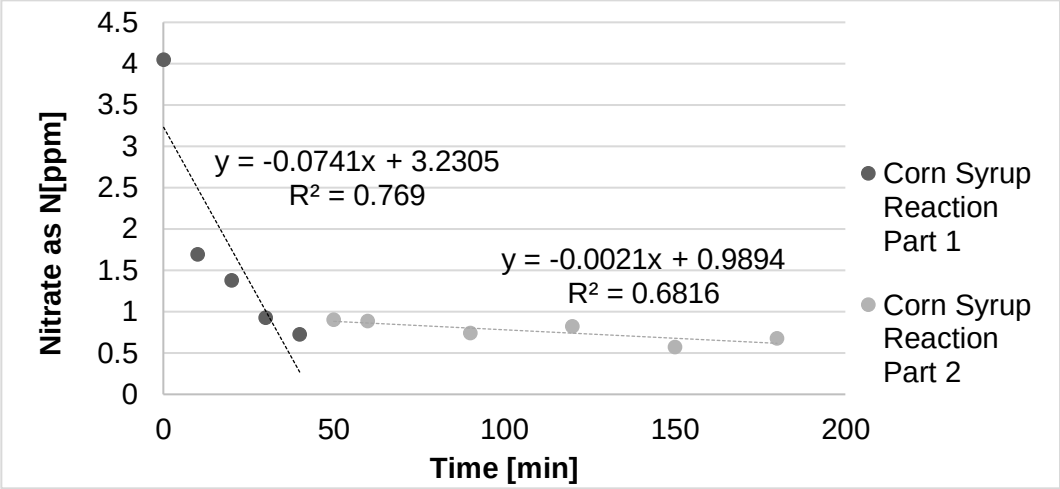


Figure 16: Corn Syrup Reactor Test Results

The COD began at 1,005 mg/L and ended at 978 mg/L as seen in the graph of COD versus time in Figure 17 below. The difference between the highest and lowest COD values was 82 mg/L.

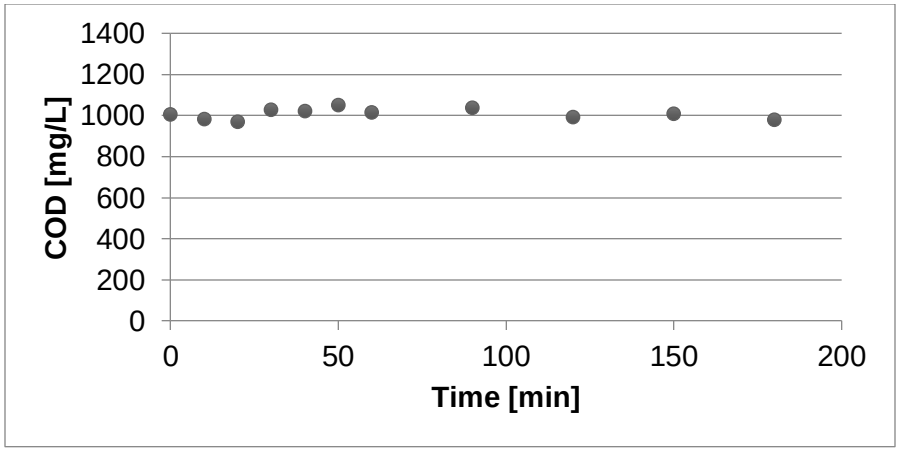


Figure 17: COD over Time for Corn Syrup

There is some fluctuation observed in the graph. The fluctuations and slight decreasing trend are expected to sometimes occur in the denitrification process and may be acceptable. The values observed are mainly stable without significant change or decreases. Corn syrup had the smallest fluctuation in COD over time out of all the final tests; this is desirable. UBWPAD would have to ensure any effects on COD are not detrimental to their process.

The hourly pH and reactor temperature are displayed in Table 7 below. The pH started at 7.53 and ended at 7.98 and hit its highest point of 8.11 during the test. The beginning pH level was slightly higher than the desired 7-7.5 range resulting in overall higher pH throughout the test. UBWPAD would have to ensure there would be no negative effects on their processes to pursue corn syrup.

Table 7: The Hourly Temperature and pH of the Final Corn Syrup Test

Hour	Reactor Temperature (°C)	pH
0	15.0	7.53
1	17.4	8.09
2	19.0	8.11
3	20.4	7.98

The temperature for the final test began at 15.0℃ and ended at 20.4℃. This increase can be expected as the wastewater is removed from the fridge and adjusts to room temperature.

3.3.3. Biodiesel Production Waste

For the three-hour test, 20 mg of sodium nitrate were added to the wastewater, increasing the nitrate concentration to 2.82 mg/L. Then, 6.0 microliters of biodiesel waste were added to the reactor. The changes in nitrate concentrations during the final reactor test can be seen in Figure 18 below. The overall percent decrease in nitrate was 83.0%. The calculated specific denitrification rate for biodiesel waste was -0.103 kgN/kgVSS/d. The denitrification rate of biodiesel waste compared to Micro-C, –0.053 kgN/kgVSS/d, is approximately two times faster.

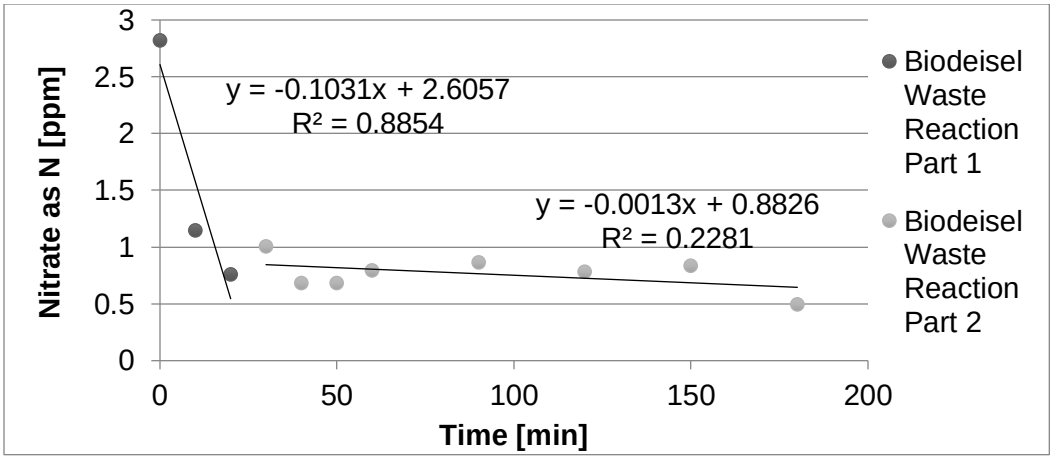


Figure 18: Biodiesel Production Waste Reactor Test Results

The changes in COD values during the 3-hour reactor test can be seen in Figure 19. The COD of the reactor with the carbon source started at a value of 1,911 mg/L and ended at a value of 1,521 mg/L.

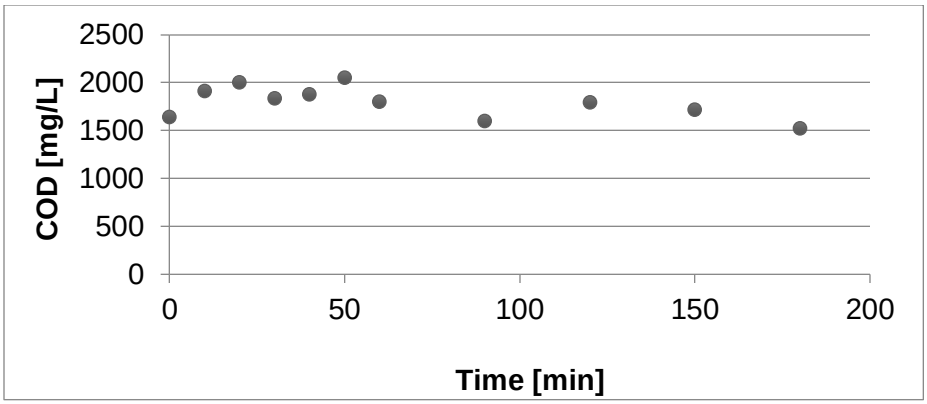


Figure 19: COD over Time for Biodiesel Production Waste

The pH and temperature values of the reactor are recorded in. The temperature during the experiment increased from 11.7°C to 22.0°C as the reactor adjusted to room temperature. The pH changed from 7.63 to 8.40. The large pH change is expected due to the strong base (KOH) present in the waste sample; however, this may be problematic for the plant and a pH adjustment chemical may be needed. The specific hourly temperatures and pH are found in Table 8.

Table 8: The Hourly Temperature and pH of the Biodiesel Production Waste Test

Hour	Reactor Temperature (°C)	pH
0	11.7	7.63
1	18.0	7.56
2	20.0	8.34
3	22.0	8.40

During the reactor tests, it was difficult to pipette the correct amount of biodiesel waste into the Erlenmeyer flask due to its high viscosity. If biodiesel waste is selected there may be some design considerations that must be taken into account, further design recommendations are discussed below.

3.3.4. Sugar Production Waste

As seen in Figure 20, the reaction mostly occurs within the first 40 minutes and then fluctuates around 0.75 ppm. The denitrification rate was approximately –0.039 kgN/kgVSS/d when the nitrate concentration in the reactor depleted from 2.8 ppm to 0.8 ppm. The reaction rate of Micro-C was –0.053 kgN/kgVSS/d. Sugar denitrifies the wastewater at a slower rate than Micro-C. The slower reaction rate may be of concern to UBWPAD depending on the time within the anoxic reactor.

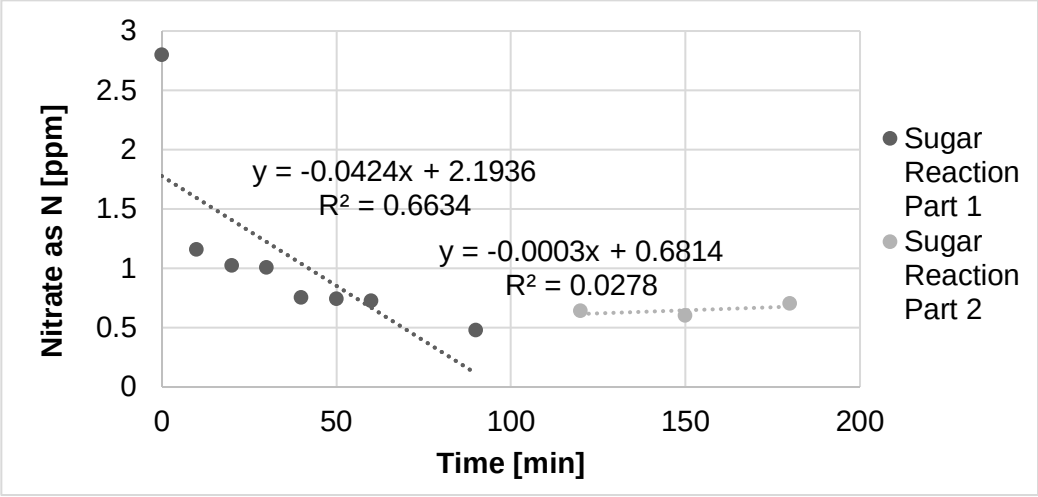


Figure 20: Sugar Waste Reactor Test Results

The COD stayed within a range between 980.0-1020 mg/L as seen in Figure 21.

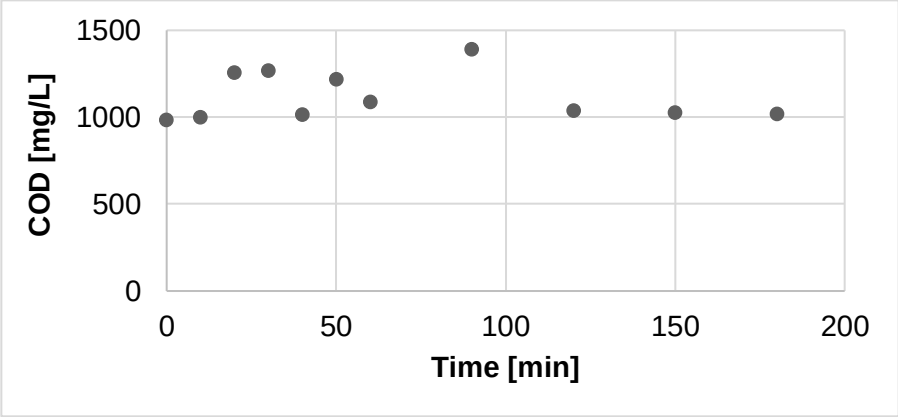


Figure 21: COD over Time for Sugar Waste

The pH and temperature of the reactor were examined. The temperature changed from 15.2°C to 22.0°C throughout the test. The change occurred because the wastewater was taken out of the refrigerator and reached room temperature as time moved on. The pH increased by 0.54. UBWPAD will need to examine the changes in both the temperature and pH to see if the reaction could be problematic for the plant. Table 9 contains the data collected for the change in reactor temperature and pH.

Table 9: The Hourly Temperature and pH of the Sugar Test

Hour	Reactor Temperature (°C)	pH
0	15.2	7.54
1	18.6	7.75
2	20.6	7.97
3	22.0	8.08

The temperature needs to be examined because high temperatures in the summer with a potential increase in temperature from the reaction may cause the wastewater to evaporate off harmful chemicals depending on what type of waste is flowing through the system. The pH is important because phosphorus removal occurs after nitrate removal in the plant. Change in the pH could affect the results of other necessary nutrient removal before the treated wastewater enters the river.

3.3.5. Chemical Manufacturing Waste: DOW Chemical (Glycerin)

DOW chemical waste was also selected to undergo final testing. Figure 22 shows the concentrations of nitrate during the final test for DOW chemical waste.

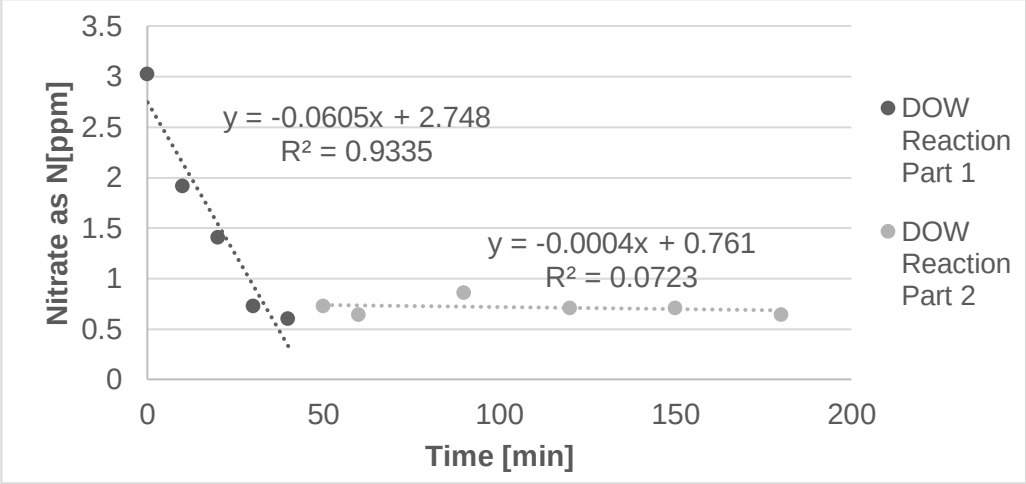


Figure 22: DOW Chemical Waste Reactor Test Results

The concentration of nitrate begins at 3.0 ppm and at the end of the final three-hour test the concentration of nitrate decreased to 0.64 ppm. The nitrate concentration is lowest after 40 minutes, where it is 0.60 ppm. DOW chemical waste's denitrification rate was calculated to be –0.052 kgN/kgVSS/d, which was very similar to Micro-C's denitrification rate of –0.053 kgN/kgVSS/d. The CODs were also measured through the final three-hour tests. Figure 23 shows the COD values during the final test.

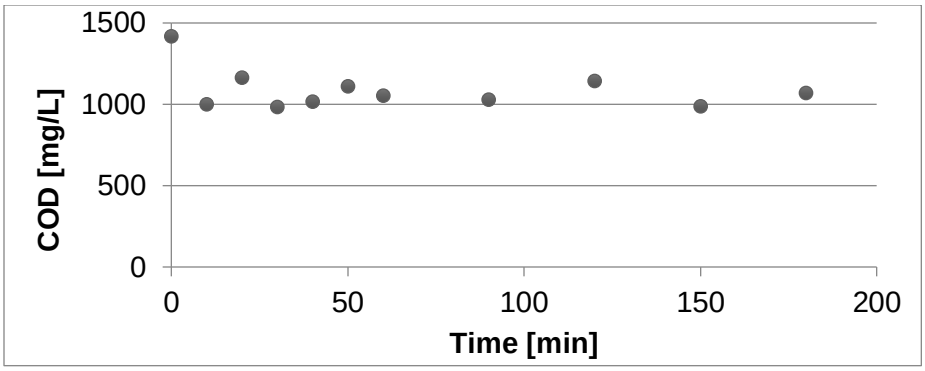


Figure 23: COD over Time for DOW Chemical Waste

The initial, and highest, COD of the water was 1,418 mg/L and remained relatively consistent throughout the test. The lowest COD value was 984.3 mg/L which occurred after 30 minutes.

The pH of the water started at 6.66 and slightly increased to 7.66 at the conclusion of the test but still remained around neutral. Temperature of the reactor were also examined. Table 10 shows the hourly reactor temperature and pH of the final DOW chemical test.

Table 10: The Hourly Temperature and pH of the DOW Chemical Waste Test

Hour	Reactor Temperature (°C)	pH
0	15.2	6.66
1	18.6	7.40
2	20.6	7.24
3	22	7.66

The glycerin would be a viable option for UBWPAD because DOW Chemical produces this waste in large quantities and currently has to pay to dispose of it. The waste has a consistent composition and DOW Chemical is willing to look into negotiations with UBWPAD so they can potentially both save money by reusing the waste.

3.4. Design

Using the data from the final tests, preliminary designs were developed for UBWPAD to implement into their denitrification treatment process. The system had a basic design of a holding tank for the carbon source, valves, piping, and a pump for each anaerobic tank to treat an average daily flow of 30 MGD of wastewater with an 8 ppm nitrate concentration. A schematic below in Figure 24 shows this setup along with pipe lengths.

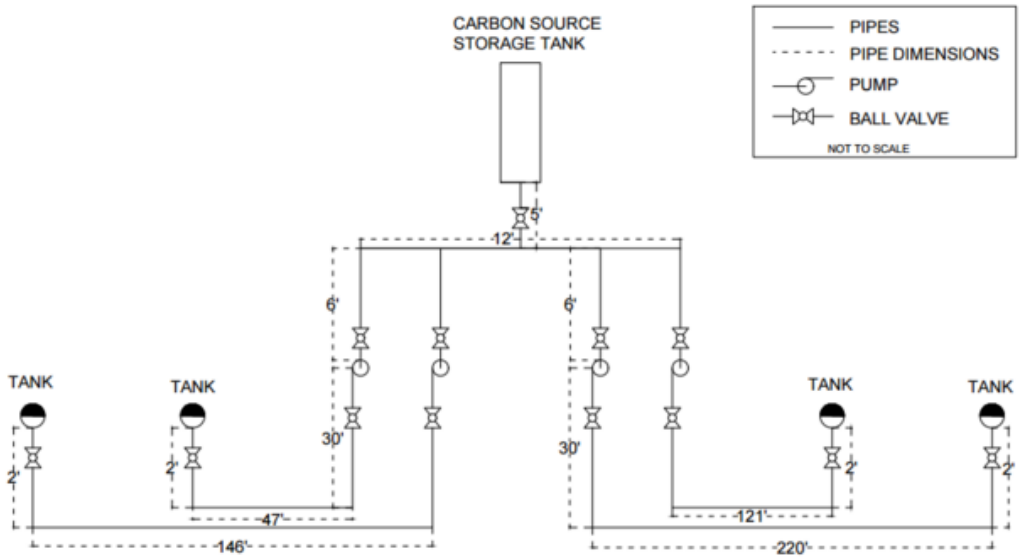


Figure 24: A P&ID of the Schematic of the Carbon Byproduct Design

The calculations for volume and flow rates of corn syrup, sugar solution, and glycerin exceeded the desired size of pump and storage tank, whereas the biodiesel production waste required pump and storage tank sizes that would fit into the scale of UBWPAD's system. Corn syrup required 66,000 gallons per month and 90 GPH, sugar solution required 72,000 gallons per month and 98 GPH, and DOW Chemical waste required 731,000 gallons per month and 982 GPH. These materials would be more expensive and would require space for larger storage tanks and pumps. Some companies, like DOW Chemical, may not be able to provide the volumes of carbon waste necessary for denitrification at UBWPAD. Biodiesel production waste required 3,300 gallons per month and 5 GPH. The biodiesel waste could operate with a significantly smaller storage volume than the others and using the desired smaller pumps. Biodiesel production waste was determined to be the most effective option for an alternative carbon source for denitrification at UBWPAD.

The LMI Series C Chemical Metering Pump C73 was chosen for the system. The LMI pump has a chemically resilient interior and durable exterior. The max output capacities of 8 GPH and 60 psi were found to be compatible with the system designed for biodiesel production waste. The average power input at maximum speed is 44 watts. The pump costs more than a peristaltic pump that could be used for the higher viscosity carbon sources. If UBWPAD chose to use a different carbon source in the future, the LMI pump could potentially continue to be used. There are other options of chemical metering pumps from LMI that could also be feasible if preferred by UBWPAD. A specification sheet in Appendix F provides additional details for the LMI C73 pump as well as other similar pump options.

We selected chlorinated polyvinyl chloride (CPVC) to be used for all piping. CPVC was selected because it will not be affected by interaction with the solutions. Schedule 40 pipe was chosen because a higher schedule wall thickness was not needed. The pipes sizes were determined from the required flowrate and allowable pressure drop in the system. One pipe flows from the chemical storage tank to a splitter. The system then tees into four pipelines, each entering a LMI Series C Chemical Metering Pump C73, and exiting out to one of the four anaerobic tanks. The flow will discharge from each pump and the pipes will run at a ten feet increase in elevation above the walkway area and then drop back down twelve feet to the denitrification tanks. Each pipe discharges to the middle of each denitrification tank and discharges two feet into the tank, above the wastewater surface level. The pipes discharged above the wastewater to avoid any complications with clogging or interference and keep a steady injection flow. The total piping needed was 735 feet, the dimensions of the system can be observed in Figure 24.

Pipe diameter was determined to be one half inch for all piping throughout the system for biodiesel production waste at a velocity of 3 meters per minute. The pressure drop over the entire pipe length from friction loss was estimated to be 0.17 feet using the Hazen-Williams equation. According to CPVC pipe manufacturer Georg Fischer Harvel, this is the most commonly used method and 150 is a widely accepted constant value for the internal pipe roughness of CPVC pipes. Static head for the pump to overcome was estimated to be 10 feet.

UBWPAD currently has one 2,000-3,000 gallon tank and two 200-300 gallon tanks. Both are made of plastic and the smaller are encased in metal. This is more than adequate storage for the 750 gallons of biodiesel waste needed per week. We decided a new vessel for the design was not necessary.

Ball valves are used throughout the system. In total, eight ball valves were placed before and after each pump, to shut off if unneeded and potentially replace when necessary. One ball valve was placed before entering each of the four anaerobic tanks. One additional ball valve was placed at the exit of the biodiesel holding tank to stop and start flow of the carbon source. The ball valves had a 0.5 inch diameter to fit to the piping and are made of CPVC. These valves are available at Home Depot as well as from additional manufacturers.

The final design for biodiesel waste as a carbon source is presented in Figure 25. A Computer Aided Design (CAD) drawing was produced to display the setup. This design was a preliminary design for UBWPAD to use and adjust as needed.

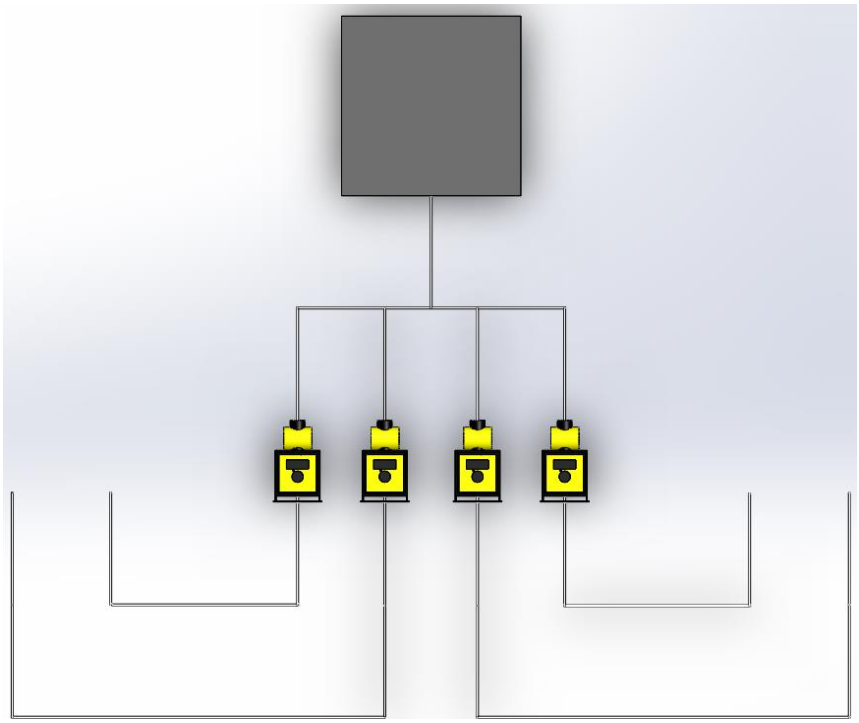


Figure 25: CAD Drawing of the Biodiesel Waste Design for UBWPAB

The process was designed for operations year round at 30 MGD of wastewater with an 8 ppm nitrate concentration. The design was made for a higher capacity than the seasonal treatment of nitrate levels usually experienced by UBWPAD.

3.5 Cost Analysis

Once the design for the biodiesel waste denitrification system was completed, the capital cost was determined. The equipment costs are approximate values from online sources and company representatives. The pump is the LMI Chemical Metering C73 Pump, customer services provided pricing per individual pump. The piping cost was found from manufacturer Georg Fischer Harvel. The ball valves' prices were taken from Home Depot. The equipment costs can be seen in Table 11 below. Four pumps were costed for the design; one for each tank, and usually UBWPAD will have three tanks operational, allowing one pump to serve as a backup if needed.

Table 11: The Cost Analysis for the Design Equipment

Equipment	Cost per measurement	Amount needed	Cost($)
Pumps	$1,600.00/pump	4 pumps	$6,400.00
Pipes	$0.20/ft	735 feet	$147.00
Ball valves	$5.30/valve	13 valves	$68.90
Total cost			$6,615.90

We determined two potential sources for the biodiesel production waste. Each source varies in distance and the cost of transportation would need to be considered for each source. The first is Northeast Biodiesel, located 64.1 miles away from UBWPAD, and the next is located 41.7 miles away at Mass Biofuel. Transportation costs for UBWPAD will depend on which company pays for the cost, whether a truck is already available, and other factors, including fuel cost. Both potential companies would need to be contacted by UBWPAD and negotiated with. Whether there is enough waste available, the manufacturer is willing to provide waste, and if there will be a cost are all factors we could not determine within this project.

4.0 Conclusions and Recommendations

Unrefined biodiesel production waste is recommended as the most effective carbon source for denitrification at UBWPAD. We recommend that UBWPAD perform additional batch reactor testing with larger volumes of wastewater and contact the desired companies that produce a biodiesel waste byproduct. Some potential biodiesel manufacturers include Northeast Biodiesel, located in Greenfield, Massachusetts and Mass Biofuel, located in Dedham, Massachusetts. We recommend contacting companies located in the state of Massachusetts to avoid the time consuming process of state approval and recycling permits. We advise UBWPAD to perform a scaled-up test on the carbon byproduct to ensure effectiveness. Compliance with Department of Transportation (DOT) regulations for transportation of the byproduct is important for UBWPAD to take into account.

If the scaled-up tests have continuous success, then a full-scale pilot test could be performed at UBWPAD. A negotiation between UBWPAD and the company of choice is necessary for a total cost. Negotiations may need to consider various factors: method of transportation, costing of carbon source and transportation, general disposal costs, and a delivery schedule. Once negotiations are reached a formal contract can be drafted and agreed upon by both parties. Refer to Appendix H for additional suggestions and advice. We developed a preliminary design that we recommend UBWPAD consider for further development.

Reference List

Acetate. (2015, October 1). Retrieved November 6, 2015, from http://pubchem.ncbi.nlm.nih.gov/compound/acetate#section=Related-Compounds-with-Annotatiohttp://pubchem.ncbi.nlm.nih.gov/compound/acetate#section=Related-Compounds-with-Annotationn

Acetone MSDS. Sciencelab.com.

"Anaerobic Digestion." *Waste Water Handbook*. Web.

Barnstable County Department of Health and Environment, Basic Constituents of Wastewater. (2015). Barnstable County Department of Health and Environment, Barnstable. Retrieved on September 8, 2015. <http://www.barnstablecountyhealth.org/resources/publications/compendium-of-information-on-alternative-onsite-septic-system-technology/basics-of-wastewater-treatment>

Boyle, Richard, and Peter Witherington. "Guidance on Evaluation of Development Proposals on Sites Where Methane and Carbon Dioxide Are Present." *Nhbc.co.uk*. National House-Building Council, Mar. 2007. Web.

Bridie´, A., Wolff, C., & Winter, M. (1979). BOD and COD of some petrochemicals. *Water Research, 13*(7), 627-630.

Bursey, Robert G. "New Industrial Uses of Dairy Products." *National Agricultural Library*. United States Department of Agriculture.

Cargill. (2013, June 20). IsoClear® 42% High Fructose Corn Syrup. Retrieved February 4, 2016, from https://www.cargillfoods.com/wcm/groups/internal/@cseg/@food/@all/documents/document/na3014966.pdf

Cherchi, C et. al., (2009). Implication of Using Different Carbon Sources for Denitrification in Wastewater Treatments.Water Environment Research, Volume 81, Issue 8.

Constantine, T. (2008, February 19). An Overview of Ammonia and Nitrogen Removal in Wastewater Treatment. Retrieved September 16, 2015.

Cormier, M., Suchecki Jr., R., Pertuit, R., Brown, D., & Cormier, T. (2010). *Compound for denitrifying wastewater*. United States Patent and Trademark Office.

Corn Naturally. (n.d.). HFCS COMPOSITION. Retrieved February 04, 2016, from http://www.cornnaturally.com/hfcs-scientific-data/HFCS-Nutritional-Equivalencies/Composition

Davis, M., & Masten, S. (2004). Wastewater Treatment. In *Principles of Environmental Engineering and Science*. New York, NY: McGraw-Hill

deBarbadillo, C. et. al.,(2008). Got Carbon? Widespread biological nutrient removal is increasing the demand for supplemental sources. Water Environment Federation http://www.webpages.uidaho.edu/ce432/WET-Got%20Carbon.pdf

De Filippis, P., Di Palma, L., Scarsella, M., & Verdone, N. (2013). Biological Denitrification of High-Nitrate Wastewaters: A Comparison Between Three Electron Donors. *Chemical Engineering Transactions, 32*, 319-324. Retrieved February 4, 2016, from http://www.aidic.it/cet/13/32/054.pdf

Dragicevic, Tibela. "The potential of dairy wastewater for denitrification". University of Zagreb, 2010. Retrieved from <file:///C:/Users/Dallen/Downloads/Mljekarstvo_29_9_2010_191_197%20(1).pdf>

Environmental Operating Solutions, MicroC Premium Carbon Sources. (2006). Environmental Operating Solutions Inc., Bourne. Retrieved September 5, 2015. http://microc.com/product/index.htmhttp://microc.com/product/index.htm http://microc.com/product/index.htm
Environmental Protection Agency. (2012, March 6). *Water: Monitoring and Assessment: 5.7 Nitrates*. Retrieved from EPA: United States Environmental Protection Agency: http://water.epa.gov/type/rsl/monitoring/vms57.cfm

Grabinska-Loniewska, A. Slomczynski T. Kanska Z. Denitrification Studies with Glycerol as a Carbon Source. Institute of Environmental Engineering, Warsaw Technical University. Retrieved October 6, 2015.

Gu, A., & Onnis-Hayden, A. (2010). PROTOCOL TO EVALUATE ALTERNATIVE EXTERNAL CARBON SOURCES FOR DENITRIFICATION AT FULL-SCALE WASTEWATER TREATMENT PLANTS. *Water Environment Research Foundation*. Retrieved August 31, 2015.

"Isopropyl Alcohol MSDS." Sciencelab.com, Inc.

"Lactic Acid". Corbion Purac, 2014. Retrieved from <http://www.lactic-acid.com/physical_properties.html>

Langeland, W. E., & Filipiak, D. J. (2016, February 4). *Food Processing Wastewater Treatment Design*. Lecture.

Liang, W. (2013). *Evaluation of an Industrial By-product Glycol Mixture as a Carbon Source for Denitrification*. Blacksburg, Virginia: Virginia Polytechnic Institute.

Ma, Y. Peng, Y. Wang S. (2007). Denitrification potential enhancement by addition of external carbon sources in a pre-denitrification process. Journal of Environmental Sciences 19(2007) 284-289. Retrieved October 2, 2015.

Mark Johnson, Personal Correspondence, September 4, 2015.

"Material Safety Data Sheet Lactic Acid." *Trade-chem.com*. Chemtrade International. Web.

MSDS Lactose." *Hummelcroton.com*. Hummel Croton. Web. 04 Feb. 2016.

Net Industries. (2015). *Chemical Oxygen Demand*. Retrieved from Net Industries: http://science.jrank.org/pages/1388/Chemical-Oxygen-Demand.html

Nutrients Review. (2015). Alcohol (Ethanol) Chemical and Physical Properties. Retrieved February 04, 2016, from http://www.nutrientsreview.com/alcohol/definition-physical-chemical-properties.html

Pretorius, C., Kilian, R., & Jannone, J. (2006). *GIVE YOUR DENITRIFICATION BUGS A SUGAR HIGH* [Scholarly project]. In *Water Environment Foundation*. Retrieved February 3, 2016.

PubChem. (2004, September 16). Sucrose. Retrieved February 04, 2016, from http://pubchem.ncbi.nlm.nih.gov/compound/sucrose#section=Color

Ridge, Tom, and Mary E. Peters. "The Methanol Alternative to Gasoline." *The New York Times*. The New York Times, 23 Feb. 2012. Web. 08 Feb. 2016.

Robertson, Steve. "Glycerol." *Inchem.org*. National Centre for Ecotoxicology & Hazardous Substances, Mar. 2002. Web.

ScienceLab. (2013). *Acetic acid MSDS*. Sciencelab.com.http://science.jrank.org/pages/1388/Chemical-Oxygen-Demand.html

ScienceLab. (2013). *Propylene Glycol MSDS*. Sciencelab.com. http://science.jrank.org/pages/1388/Chemical-Oxygen-Demand.html
Snyder, J. R., Hagerty, P. F., & Molstad, M. C. (1957, April). *Operation and Performance of Bench Scale Reactors.* Retrieved from ACS Publications: http://pubs.acs.org/doi/pdf/10.1021/ie50568a033

"Sucrose." *PubChem OPEN CHEMISTRY DATABASE*. National Center for Biotechnology Information, 30 Jan. 2016. Web. 04 Feb. 2016.

"The activated sludge system". The Wastewater Handbook, 2013. Retrieved from <http://www.wastewaterhandbook.com/documents/organic_material_metabolism/211_OMBM_COD.pdf>

Turton, Richard. *Analysis, Synthesis, and Design of Chemical Processes*. Upper Saddle River, N.J: Prentice Hall, 2003. Print.

Upper Blackstone Water Pollution Abatement District. (n.d.). *Home*. Retrieved from Upper Blackstone Water Pollution Abatement District: http://www.ubwpad.org/

"Wastewater Treatment Fact Sheet: External Carbon Sources for Nitrogen Removal." United States Environmental Protection Agency, 1 Aug. 2013

World Bank Group. "Dairy Industry". Pollution Prevention Control, 1998. Retrieved from <http://www.ifc.org/wps/wcm/connect/2668f38048855c0e8adcda6a6515bb18/dairy_PPAH.pdf?MOD=AJPERES>

Y. Fernández-Nava, E. Marañón, J. Soons, L. Castrillón, Denitrification of high nitrate concentration wastewater using alternative carbon sources, Journal of Hazardous Materials, Volume 173, Issues 1–3, 15 January 2010, Pages 682-688, ISSN 0304-3894, http://dx.doi.org/10.1016/j.jhazmat.2009.08.140.

Znanstveni, Izvorni Rad. "The Potential of Dairy Wastewater for Denitrification." *Faculty of Food Technology and Biotechnology, University of Zagreb* (n.d.): n. pag. Web. 8 Feb. 2016.

Appendices

Appendix A: Calculations

Nitrate Conversion Calculations

Standard Curve Equation: The standard curve equation was used to convert readings from the nitrate probe in millivolts to concentration of nitrate as nitrogen in parts per million. An example calculation with biodiesel waste is shown below.

$$y = -11.12\ln(x) + 129.32$$

Nitrate probe reading = 141.3 mV

$$y = -11.12\ln(x) + 129.32$$

Solve for x (nitrate as N):

$$x = e^{\left[\frac{(y-129.32)}{-11.12}\right]}$$

$$x = e^{\left[\frac{(141.3-129.32)}{-11.12}\right]}$$

$$x = 0.341\ ppm\ Nitrate\ as\ N$$

Dilution = 50% NISS to wastewater

$$\boldsymbol{x = 0.681\ ppm\ Nitrate\ as\ N}$$

Equation 9 was used to calculate the volume of each carbon source needed for complete denitrification in the reactor tests.

Equation 9: The equation used to calculate the desired volume of each carbon source for denitrification in the reactor

$$Volume\ of\ carbon\ source\ needed\ = \frac{\left(\frac{F}{M}\right)(Volume\ of\ wastewater)\left(MLVSS\ \left(\frac{mg}{L}\right)\right)}{COD\ \left(\frac{mg}{L}\right)}$$

The following table contains data used to calculate the volume of each carbon source needed for the reactor tests. Using the data, the volume of DOW needed was calculated.

Carbon source	F/M ratio	COD (mg/L)	Volume of wastewater (L)	MLVSS (mg/L)
DOW	0.035	75,725	1.6	1700
Micro-C	0.035	840,021	1.6	1700
Biodiesel waste	0.035	16,587,500	1.6	1700
Sugar	0.035	1,206,308	1.6	1700
Corn syrup	0.035	830,042	1.6	1700

$$Volume\ of\ DOW\ needed\ = \frac{(0.035)(16000\ mL)\ (1700\ mg/L)}{75{,}725\ mg/L} = \mathbf{1.26\ mL}$$

$$Volume\ of\ Micro-C\ needed\ = \frac{(0.035)(16000\ mL)\ \left(1700\frac{mg}{L}\right)}{840{,}021\frac{mg}{L}}\left(\frac{1000\ \mu L}{1mL}\right) = \mathbf{115\ \mu L}$$

$$Volume\ of\ Biodiesel\ needed\ = \frac{(0.035)(16000\ mL)\ \left(1700\frac{mg}{L}\right)}{16{,}587{,}500\frac{mg}{L}}\left(\frac{1000\ \mu L}{1mL}\right) = \mathbf{6\ \mu L}$$

$$Volume\ of\ Ethylene\ Glycol\ needed\ = \frac{(0.035)(16000\ mL)\ \left(1700\frac{mg}{L}\right)}{15{,}195\frac{mg}{L}} = \mathbf{6.3\ mL}$$

$$Volume\ of\ Elite\ windshield\ needed\ = \frac{(0.035)(16000\ mL)\ \left(1700\frac{mg}{L}\right)}{1{,}032\frac{mg}{L}} = \mathbf{92\ mL}$$

The calculation for sugar was slightly altered because the mass in grams was needed, not the volume. To determine the amount of grams needed, the theoretical volume needed was converted to grams by multiplying the number by the density of sugar,

$$Grams\ of\ Sugar\ needed\ = \frac{(0.035)(16000\ mL)\ \left(1700\frac{mg}{L}\right)}{1206308\frac{mg}{L}}\left(\frac{1.59\ g}{1mL}\right) = \mathbf{0.31\ g}$$

$$Volume\ of\ Corn\ syrup\ needed\ = \frac{(0.035)(16000\ mL)\ \left(1700\frac{mg}{L}\right)}{830042\frac{mg}{L}}\left(\frac{1000\ \mu L}{1mL}\right) = \mathbf{120\ \mu L}$$

The standard denitrification rate was calculated for each final reactor test. The MLSS of the wastewater was measured before and after the test. The average of the two MLSS values was used to represent the MLSS during the test. The MLVSS value was calculated by multiplying the MLSS by 0.8. The slope of the first line for each reactor curved was also used to calculate SDNR. The SDNR and MLVSS equations can be seen below, where $slope_O$ is equal to the initial slope.

$$MLVSS = \left[\left(\frac{MLSS_O - MLSS_F}{2}\right)(0.8)\right]$$

$$SDNR = (1440\frac{\text{min}}{\text{day}})Slope_O/MLVSS$$

The SDNR and MLVSS calculations for each carbon source that underwent final testing can be seen below.

$$MLVSS\ DOW = \left[\left(\frac{2754\frac{mg}{L} - 1400\frac{mg}{L}}{2}\right)(0.8)\right] = \mathbf{1661.6\frac{mg}{L}\ VSS}$$

$$SDNR\ DOW = \frac{1440\frac{min}{day}\left(-.0741\ mg\frac{N}{min}\right)}{1{,}661.6\frac{mg}{L}VSS} = \frac{\mathbf{-.06422\ mg\ N}}{\mathbf{mg\ VSS * day}}$$

$$MLVSS\ Biodiesel\ waste = \left[\left(\frac{2168\frac{mg}{L} - 1430\frac{mg}{L}}{2}\right)(0.8)\right] = \mathbf{1799\frac{mg}{L}\ VSS}$$

$$SDNR\ Biodiesel\ waste\ = \frac{1440\frac{min}{day}\left(-.1031\ mg\frac{N}{min}\right)}{1{,}799\frac{mg}{L}VSS} = \frac{\mathbf{-.10316\ mg\ N}}{\mathbf{mg\ VSS * day}}$$

$$MLVSS\ Sugar = \left[\left(\frac{2502\frac{mg}{L} - 1396\frac{mg}{L}}{2}\right)(0.8)\right] = \mathbf{1559.2\frac{mg}{L}\ VSS}$$

$$SDNR\ Sugar\ = \frac{1440\frac{min}{day}\left(-.0424\ mg\frac{N}{min}\right)}{1{,}559.2\frac{mg}{L}VSS} = \frac{\mathbf{-.03916\ mg\ N}}{\mathbf{mg\ VSS * day}}$$

$$MLVSS\ Micro - C\left[\left(\frac{2502\frac{mg}{L} - 1202\frac{mg}{L}}{2}\right)(0.8)\right] = \mathbf{1481.6\frac{mg}{L}\ VSS}$$

$$SDNR\ Micro - C = \frac{1440\frac{min}{day}\left(-.1155\ mg\frac{N}{min}\right)}{1{,}481.6\frac{mg}{L}VSS} = \frac{\mathbf{-.11226\ mg\ N}}{\mathbf{mg\ VSS * day}}$$

$$MLVSS\ Corn\ syrup\left[\left(\frac{2502\frac{mg}{L} - 1224\frac{mg}{L}}{2}\right)(0.8)\right] = \mathbf{1863\frac{mg}{L}\ VSS}$$

$$SDNR\ Corn\ syrup\ \frac{1440\frac{min}{day}\left(-.1333\ mg\frac{N}{min}\right)}{1{,}863\frac{mg}{L}VSS} = \frac{\mathbf{-.10303\ mg\ N}}{\mathbf{mg\ VSS * day}}$$

Flow Rate Calculations

Volume WW = 160 MGD = 605,665.6 L
F/M = 0.035
MLVSS = 1,700 mg/L
COD DOW Chemical Waste = 75,725 mg/L

$$Volume\ Carbon\ Source = \frac{\frac{F}{M} * V_{WW} * MLVSS}{COD}$$

$$Volume\ Carbon\ Source = \frac{0.035 * 605{,}665.6\ L/day * 1{,}700\ mg/L}{75{,}725\ mg/L}$$

$$Volume\ Carbon\ Source\ (gal) = 89{,}230\ L/day * \frac{0.264\ gal}{1\ L}$$

$$\boldsymbol{Volume\ Carbon\ Source\ (gal) = 3{,}572\ \frac{gal}{day} = 982\ \frac{gal}{hour} = 16.4\ \frac{gal}{min}}$$

Volume WW = 160 MGD = 605,665.6 L
F/M = 0.035
MLVSS = 1,700 mg/L
COD Biodiesel Waste = 16,587,500 mg/L

$$Volume\ Carbon\ Source = \frac{\frac{F}{M} * V_{WW} * MLVSS}{COD}$$

$$Volume\ Carbon\ Source = \frac{0.035 * 605{,}665.6\ L/day * 1{,}700\ mg/L}{16{,}587{,}500\ mg/L}$$

$$Volume\ Carbon\ Source\ (gal) = 407\ L/day * \frac{0.264\ gal}{1\ L}$$

$$\boldsymbol{Volume\ Carbon\ Source\ (gal) = 108\ \frac{gal}{day} = 4.48\ \frac{gal}{hour} = 0.075\ \frac{gal}{min}}$$

Volume WW = 160 MGD = 605,665.6 L
F/M = 0.035
MLVSS = 1,700 mg/L
COD Sugar = 1,206,308 mg/L
Density (ρ) Sugar = 1,590,000 mg/L

$$Volume\ Carbon\ Source = \frac{\frac{F}{M} * V_{WW} * MLVSS}{COD}$$

$$Volume\ Carbon\ Source = \frac{0.035 * 605{,}665.6\ L/day * 1{,}700\ mg/L}{1206308\ mg/L}$$

$$Volume\ Carbon\ Source\ (gal) = 5{,}601\ L/day$$

$$Mass\ Carbon\ Source = \rho * V_{CS}$$

$$Mass\ Carbon\ Source = 1{,}590{,}000 \frac{mg}{L} * 5{,}601\ L$$

$$Mass\ Carbon\ Source = 8{,}906{,}151{,}158\ mg$$

$$Concentration = \frac{8{,}906151{,},158\ mg}{605{,}665.6\ L}$$

$$Concentration = 78.4\ mg/L$$

Qw = 160 MGD
Cw = 78.4 mg/L
Cs = 1,000,000 mg/L

$$Qw * Cw = Qs * Cs$$

$$Qs = \frac{Qw * Cw}{Cs}$$

$$Qs = \frac{160\ MGD * 78.4 mg/L}{1{,}000{,}000\ mg/L}$$

$$\boldsymbol{Qs = 2{,}353 \frac{gal}{day} = 1.63 \frac{gal}{min}}$$

Volume WW = 160 MGD = 605,665.6 L
F/M = 0.035
MLVSS = 1,700 mg/L
COD Corn Syrup = 830,041.5 mg/L

$$Volume\ Carbon\ Source = \frac{\frac{F}{M} * V_{WW} * MLVSS}{COD}$$

$$Volume\ Carbon\ Source = \frac{0.035 * 605{,}665.6\ L/day * 1{,}700\ mg/L}{83{,}0041.5\ mg/L}$$

$$Volume\ Carbon\ Source\ (gal) = 8{,}141\ L/day * \frac{0.264\ gal}{1\ L}$$

$$\boldsymbol{Volume\ Carbon\ Source\ (gal) = 2150\ \frac{gal}{day} = 89.6\frac{gal}{hour} = 1.49\ \frac{gal}{min}}$$

Volume WW = 160 MGD = 605,665.6 L
F/M = 0.035
MLVSS = 1,700 mg/L
COD Micro-C = 840,021 mg/L

$$Volume\ Carbon\ Source = \frac{\frac{F}{M} * V_{WW} * MLVSS}{COD}$$

$$Volume\ Carbon\ Source = \frac{0.035 * 605{,}665.6\ L/day * 1{,}700\ mg/L}{840{,}021\ mg/L}$$

$$Volume\ Carbon\ Source\ (gal) = 8{,}044\ L/day * \frac{0.264\ gal}{1\ L}$$

$$\boldsymbol{Volume\ Carbon\ Source\ (gal) = 2{,}125\ \frac{gal}{day} = 88.5\frac{gal}{hour} = 1.48\ \frac{gal}{min}}$$

Pipe Diameter Calculation

$$Q = Flowrate$$
$$A = Area$$
$$v = velocity$$
$$d = diameter$$
$$Q = \frac{gallons}{minute} \times 0.00378541\ \frac{Meters}{Gallon} = \frac{Meters}{Minute}$$
$$v = meters/minute$$
$$A = \frac{Q}{v} = square\ meters$$
$$d = 2 \times \sqrt{\frac{A}{\pi}} = m$$

$$d = m \times \frac{100cm}{m} \times \frac{0.393701\ inch}{cm} = inches$$

Pressure Drop

$$L = Pipe\ length(\text{ft})$$
$$g = flowrate(\frac{gal}{\text{min}})$$
$$d = diameter(inches)$$
$$C = 150$$
$$L = 735\ feet$$
$$f(per\ 100\ feet) = 0.2083 \times (\frac{100}{C})^{1.852} \times \frac{g^{1.852}}{d^{4.365}}$$
$$f = f(per\ 100\ ft) \times L$$

Static Head

$$Static\ head = Discharge\ head - suction\ head$$

Appendix B: Raw Data

Raw Data						
Preliminary						
Carbon Source	**Dow Chemical Waste**	**Antifreeze-Ethylene Glycol**	**Elite Windshield-methanol**	**Micro-C**	**Biodiesel Waste**	**Sugar**
Date tested	2/16/16	2/17/16	2/18/16	2/19/16	2/19/16	2/23/16
Time	3:25PM	9:23AM	3:26PM	9:18AM	11:32AM	11:17AM
COD of Carbon Source	75725	15195	1032.25	840021	16587500	1206308
Amount of Carbon Source Added	1.3mL	6.3mL	92mL	115microL	6microL	0.13g
Amount $NaNO_3$ Added (mg)	10	9.9	10.1	10.3	10.7	14
pH Start	6.75	6.95	7.07	6.97	6.86	6.71
Start Reactor Temperature (C)	10	9	11.4	11.6	11.6	9
Start COD (mg/L)	1233.23	1908.25	2019	2650	2455	2287.5
Start Nitrate(ppm)	5.15	4.08	3:26PM	4.34	3.828	4.5
Start Nitrate Temp (C)	23	22.6	22.2	22.9	25.7	23
pH End	7.61	7.53	7.7	7.31	7.34	7.43
End Reactor Temp (C)	18.1	17.4	18.6	19.8	19.5	19.3
End COD (mg/L)	1125.75	3591.5	3095.5	2845	2541	2292.5
End Nitrate (ppm)	1.04	2.31	1.44	0.84	0.646	0.62
End Nitrate Temp (C)	21	23.7	23.4	25.3	26.4	25.7

Final Test Raw Data					
Carbon Source	**Dow Chemical Waste**	**Micro-C**	**Biodiesel Waste**	**Sugar**	**Corn Syrup**
Date tested	2/24/06	2/26/16	3/4/16	3/2/06	3/3/16
Time	11:29AM	9:50AM	11:19AM	10:27AM	11:36AM
COD of Carbon Source	75725	840021	16587500	1206308	830041.5
Amount of Carbon Source Added	1.3mL	115microL	6microL	0.13g	120microL
Amount $NaNO_3$ Added (mg)	16.2	15.6	20.2	17.6	26
pH start	6.66	6.9	7.63	7.54	7.53
Start Reactor Temp (C)	10	9.6	11.7	15.2	15
Start COD (mg/L)	1417.75	2048.5	1642.75	983.5	1005.75
Start Nitrate (ppm)	3.03	3.969	2.82	2.795	4.041
Start Nitrate Temp (C)	22	26.6	25	30.6	27.2
10min COD (mg/L)	999.5	1975.25	1910.5	999	981
10min Nitrate (ppm)	1.92	2.077	1.147	1.158	1.689
10min Nitrate Temp (C)	24	26	25.3	28	28
20min COD (mg/L)	1162.5	2124.75	2006.5	1257	968
20min Nitrate (ppm)	1.41	1.659	0.759	1.021	1.373
20min Nitrate Temp (C)	23.6	26.6	26.2	27.5	25
30min COD (mg/L)	984.25	1991	1836.25	1268.75	1027.75
30min Nitrate (ppm)	0.73	1.544	1.003	1.003	0.925
30min Nitrate Temp (C)	24	25.4	26	27.3	24.7
40min COD (mg/L)	1017	2052	1877.75	1014	1022
40min Nitrate (ppm)	0.6	1.147	0.681	0.752	0.719
40min Nitrate Temp (C)	23.8	25.4	27	26	25.8

Final Test Raw Data					
Carbon Source	**Dow Chemical Waste**	**Micro-C**	**Biodiesel Waste**	**Sugar**	**Corn Syrup**
50min COD (mg/L)	1111.5	2009.75	2050.75	1217	1050
50min Nitrate (ppm)	0.732	0.745	0.681	0.738	0.9
50min Nitrate Temp (C)	24	27.9	26	26.6	25.4
60min COD (mg/L)	1052.75	2160.75	1800	1086.5	1014
60min Nitrate (ppm)	0.639	1.03	0.763	0.725	0.884
60min Nitrate Temp (C)	25.4	29	26.2	28.6	25.7
pH 1hr	7.4	7.2	7.56	7.75	8.09
1hr Reactor Temp	17.4	15.4	18	18.6	17.4
1hr 30min COD (mg/L)	1027.75	1661.5	1602.25	1391.5	1035.75
1hr 30min Nitrate (ppm)	0.86	1.03	0.86	0.475	0.738
1hr 30min Nitrate Temp (C)	24.6	25.5	25.5	26.8	25.2
pH 2hr	7.4	7.31	8.34	7.97	8.11
2hr Reactor Temp	19.6	18.5	20	20.6	19
2hr COD (mg/L)	1141.5	2000	1794.5	1036.25	991.5
2hr Nitrate (ppm)	0.712	0.7	0.779	0.639	0.815
2hr Nitrate Temp (C)	25	26.6	25.6	26.4	23.6
2hr 30min COD (mg/L)	987.5	2012.75	1716.5	1925.25	1008.25
2hr 30min Nitrate (ppm)	0.706	1.463	0.83	0.6	0.564
2hr 30min Nitrate Temp (C)	25	26.4	25.6	26.4	26
pH 3hr	7.66	7.34	8.4	8.08	7.98
3hr Reactor Temp	21.4	20.6	22	22	20.4
3hr COD (mg/L)	1070.75	2096	1520.5	1016.25	978
3hr Nitrate (ppm)	0.639	1.147	0.493	0.7	0.675
3hr Nitrate Temp (C)	26	27	24.7	26.3	26.1
Start MLVSS	2754	2502	2168	2502	2502
End MLVSS	1400	1202	1430	1396	1224

Appendix C: COD Standard Curve

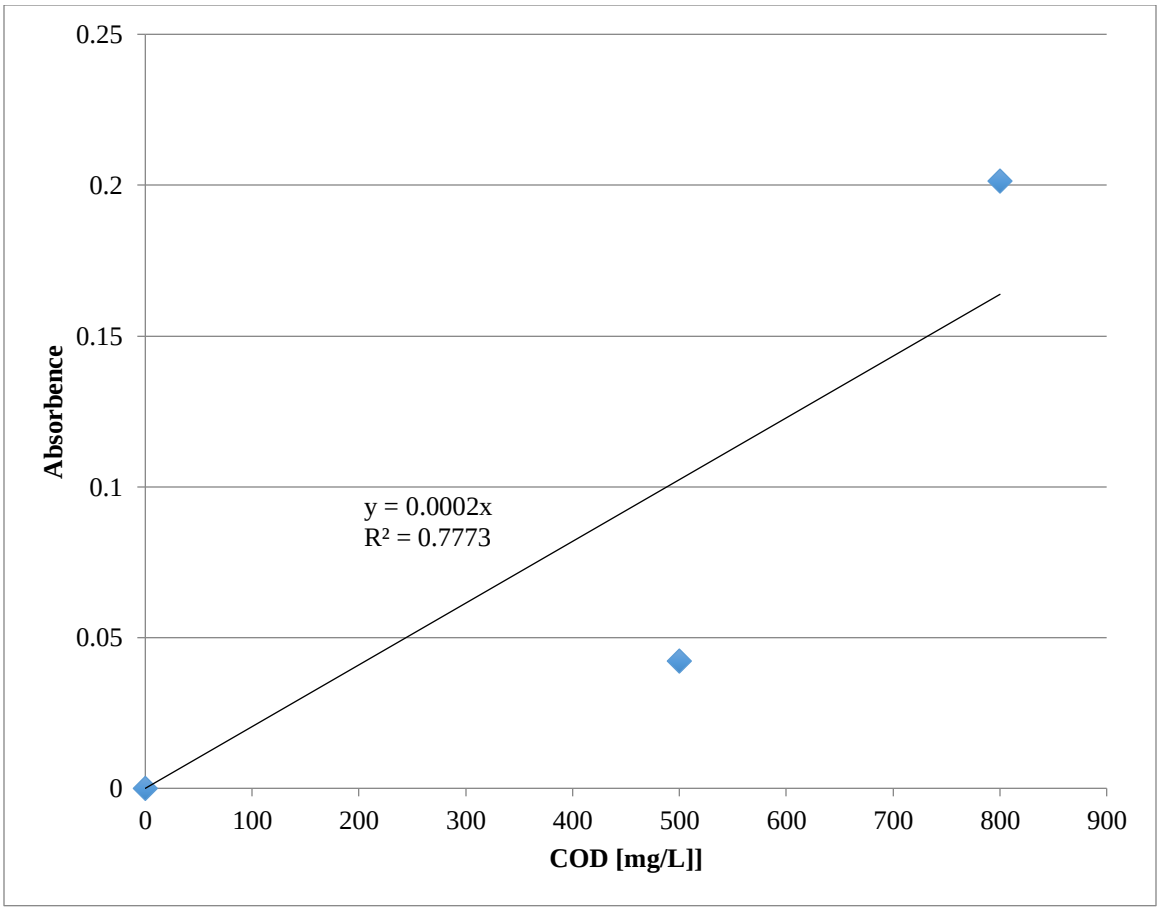


Figure 26: COD Standard Curve

Appendix D: Nitrate Calibration Curve

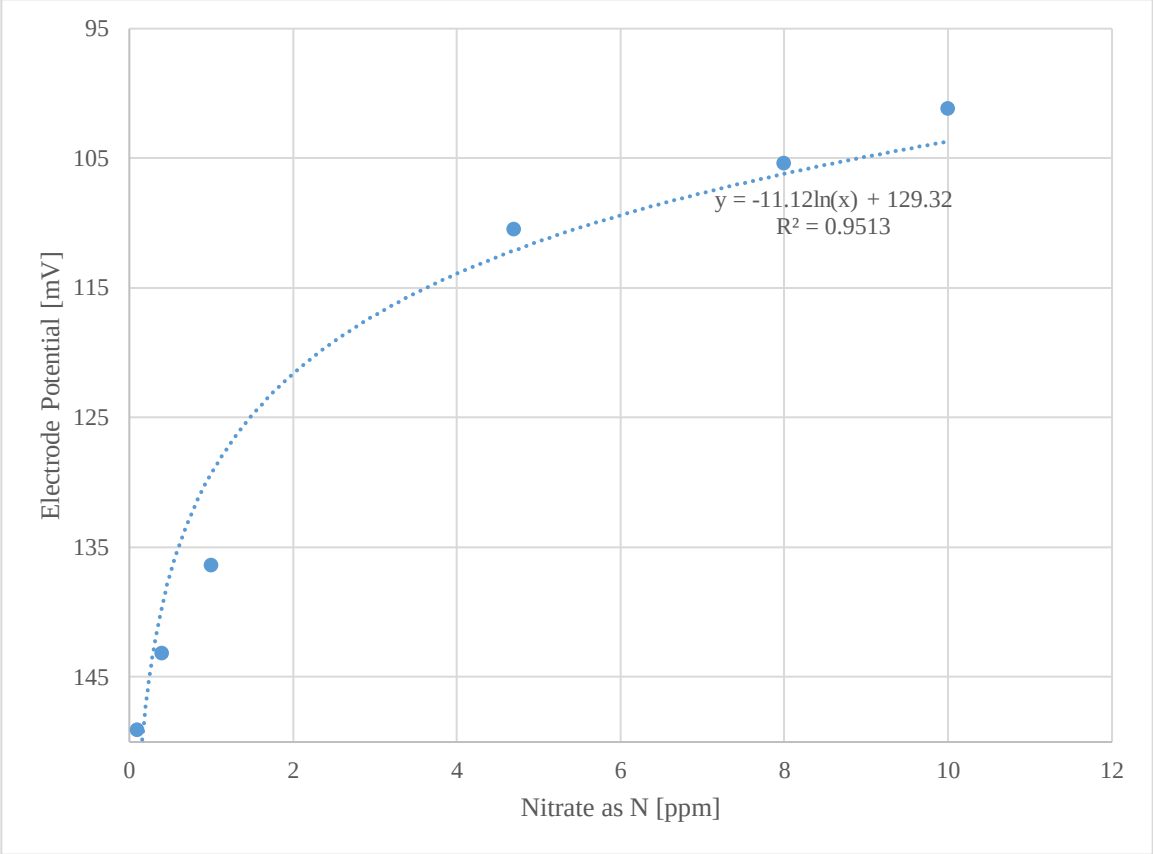


Figure 27: Nitrate Calibration Curve

Appendix E: C Series Pump Data Sheet

Data Sheet Series C

Electronic Metering Pumps

Configuration Data

Model C92 | 1 | - | 363SI

Control & Output Code with Standard Liquid End

Manual Control
Speed (stroking frequency) and stroke length manually adjustable.

C10	1.3 GPH	(4.9 l/h)	300 psi	(20.7 Bar)
C11	2.5 GPH	(9.5 l/h)	150 psi	(10.3 Bar)
C12	4.0 GPH	(15.1 l/h)	100 psi	(6.9 Bar)
C13	8.0 GPH	(30 l/h)	60 psi	(4.1 Bar)
C14	20 GPH	(76 l/h)	25 psi	(1.7 Bar)

Instrument Responsive/Manual Control
Manual adjustment features of C1 Series plus switch conversion to external control for automatic systems.

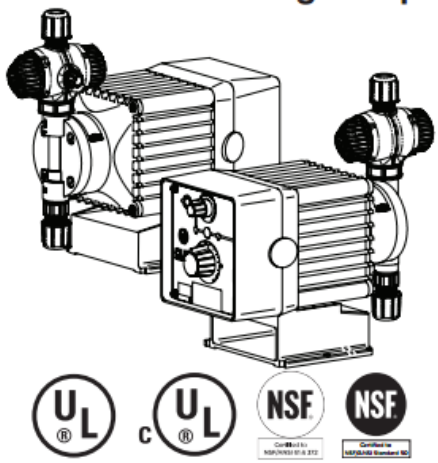
C70	1.3 GPH	(4.9 l/h)	300 psi	(20.7 Bar)
C71	2.5 GPH	(9.5 l/h)	150 psi	(10.3 Bar)
C72	4.0 GPH	(15.1 l/h)	100 psi	(6.9 Bar)
C73	8.0 GPH	(30 l/h)	60 psi	(4.1 Bar)
C74	20 GPH	(76 l/h)	25 psi	(1.7 Bar)
C76*	4.0 GPH	(15.1 l/h)	175 psi	(12.1 Bar)
C77*	10 GPH	(38 l/h)	80 psi	(5.5 Bar)
C78*	25 GPH	(95 l/h)	30 psi	(2.07 Bar)
C90	1.3 GPH	(4.9 l/h)	300 psi	(20.7 Bar)
C91	2.5 GPH	(9.5 l/h)	150 psi	(10.3 Bar)
C92	4.0 GPH	(15.1 l/h)	100 psi	(6.9 Bar)
C93	8.0 GPH	(30 l/h)	60 psi	(4.1 Bar)
C94	20 GPH	(76 l/h)	25 psi	(1.7 Bar)

Voltage Code

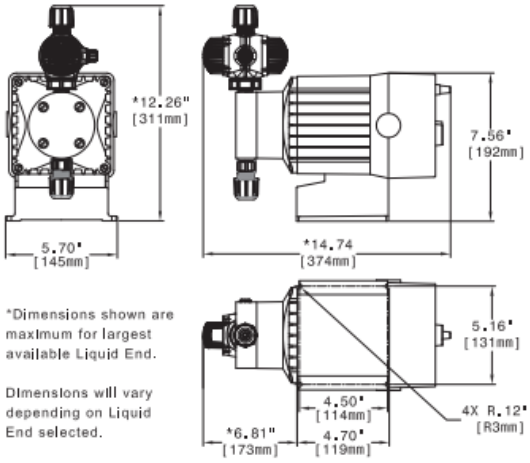
1 ------ 120 VAC US Plug
2 ------ 240 VAC US Plug
3 ------ 220-240 VAC DIN Plug
5 ------ 240-250 VAC, UK Plug
6 ------ 240-250 VAC, AUST/NZ Plug
7 ------ 220-240 VAC, SWISS Plug

Liquid End

See next page for complete liquid end specifications and selection.



Dimensions



*Dimensions shown are maximum for largest available Liquid End.

Dimensions will vary depending on Liquid End selected.

Specifications

Series	Strokes Per Minute (Adjustable) Min	Max	Stroke Length (Adjustable) Recommended Minimum	Average Input Power @ Max Speed	Shipping Weight
C10, C70, C90 C11, C71, C91 C12, C72, C92 C13, C73, C93 C14, C74, C94	1	100	10%	44 watts	20 lbs (9.1 kg)
C76** C77** C78**	1	100	10%	87 watts	28 lbs (12.7 kg)

** Not UL or CUL Approved

LMI

201 Ivyland Road
Ivyland, PA 18974 USA
TEL: (215) 293-0401
FAX: (215) 293-0445
http://www.lmipumps.com

Replaces same of Rev.K 2/2012
1712.L 11/2014

Standard Liquid End Configuration Data & Materials of Construction

Drive Assembly	Liquid End No.	Size Code	Materials of Construction: Head & Fittings	Balls	Liquifram™	Check Valve	Accessory	Tubing & Connections: Discharge	Suction
C90, C70 ☐ -	498SP	0.9	PVC	Ceramic	Fluorofilm™	PVDF/PTFE	4FV	Pipe 1/2" NPT M	
C10 ☐ -	297	0.9	316 S.S.	316 S.S.	Fluorofilm™	316 S.S.		Pipe 1/4" NPT M	
C92 ☐ - C91 ☐ - C72 ☐ - C71 ☐ - C12 ☐ - C11 ☐ -	468SI†	1.8	PVC/PVC	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	PE .375" O.D.	
	460SI†	1.8	Acrylic/PVC	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	PE .375" O.D.	
	469SI†	1.8	Acrylic/PVDF	PTFE	Fluorofilm™	PVDF/Polypret®	4FV	PE .375" O.D.	
	368SI†	1.8	PVC/PVC	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	PE .375" O.D.	
	362SI†	1.8	PVDF/PVDF	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	PE .375" O.D.	
	363SI†	1.8	PVDF/PVDF	Ceramic	Fluorofilm™	PVDF/PTFE	4FV	PE .375" O.D.	
	465SI†	1.8	Polypropylene	Ceramic	Fluorofilm™	PVDF/PTFE	4FV	PE .375" O.D.	
	75HV	1.8	Polypropylene	316 S.S.	Fluorofilm™	PTFE		PE .5" O.D. Vinyl .938" O.D.	
	76HV	1.8	Acrylic/PP	316 S.S.	Fluorofilm™	Viton®		PE .5" O.D. Vinyl .938" O.D.	
	277	1.8	316 S.S.	316 S.S.	Fluorofilm™	316 S.S.		Pipe 1/4" NPT M	
C93 ☐ - C73 ☐ - C13 ☐ -	312SI#†	3.0	PVDF/PVDF	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	PE .5" O.D.	
	313SI#†	3.0	PVDF/PVDF	Ceramic	Fluorofilm™	PVDF/PTFE	4FV	PE .5" O.D.	
	318SI#†	3.0	PVC/PVC	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	PE .5" O.D.	
	410SI#†	3.0	Acrylic/PVC	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	PE .5" O.D.	
	415SI#†	3.0	Polypropylene	Ceramic	Fluorofilm™	PVDF/PTFE	4FV	PE .5" O.D.	
	418SI#†	3.0	PVC/PVC	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	PE .5" O.D.	
	419SI#†	3.0	Acrylic/PVDF	PTFE	Fluorofilm™	PVDF/Polypret®	4FV	PE .5" O.D.	
	20	3.0	Acrylic/PVC	Ceramic	Fluorofilm™	Viton®		PE .5" O.D.	
	20HV	3.0	Acrylic/PP	316 S.S.	Fluorofilm™	Viton®		PE .5" O.D. Vinyl .938" O.D.	
	20S	3.0	Acrylic/PVC	Ceramic	Fluorofilm™	Viton®	4FV	PE .5" O.D. Vinyl .5" O.D.	
	24	3.0	PVC	Ceramic	Fluorofilm™	PTFE		Pipe 1/2" NPT M	
	25HV	3.0	Polypropylene	316 S.S.	Fluorofilm™	PTFE		PE .5" O.D. Vinyl .938" O.D.	
	26	3.0	PVC	Ceramic	Fluorofilm™	Viton®		PE .5" O.D.	
	26S	3.0	PVC	Ceramic	Fluorofilm™	Viton®	4FV	PE .5" O.D.	
	27	3.0	316 S.S.	316 S.S.	Fluorofilm™	PTFE		Pipe 1/2" NPT M	
	29	3.0	UHMW PE	Ceramic	Fluorofilm™	Viton®		PE .5" O.D.	
C94 ☐ - C78 ☐ - C74 ☐ - C14 ☐ -	30	6.0	Acrylic/PVC	Ceramic	Fluorofilm™	PTFE		PE .5" O.D. Vinyl .5" O.D.	
	34	6.0	PVC	Ceramic	Fluorofilm™	PTFE		Pipe 1/2" NPT M	
	35P	6.0	Polypropylene	Ceramic	Fluorofilm™	PTFE		Pipe 1/2" NPT M	
	35T	6.0	Polypropylene	Ceramic	Fluorofilm™	PTFE		PE .5" O.D.	
	36	6.0	PVC	Ceramic	Fluorofilm™	PTFE		PE .5" O.D.	
	37	6.0	316 S.S.	316 S.S.	Fluorofilm™	PTFE		Pipe 1/2" NPT M	
C76 ☐ -	468SP	1.8	PVC/PVC	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	Pipe 1/2" NPT M	
	74S	1.8	PVC	Ceramic	Fluorofilm™	PTFE	4FV	Pipe 1/4" NPT M	
	277	1.8	316 S.S.	316 S.S.	Fluorofilm™	316 S.S.		Pipe 1/4" NPT M	
C77 ☐ -	20	3.0	Acrylic/PVC	Ceramic	Fluorofilm™	Viton®		PE .5" O.D.	
	20HV	3.0	Acrylic/PP	316 S.S.	Fluorofilm™	Viton®		PE .5" O.D. Vinyl .938" O.D.	
	20S**	3.0	Acrylic/PVC	Ceramic	Fluorofilm™	Viton®	4FV	PE .5" O.D. Vinyl .5" O.D.	
	24	3.0	PVC	Ceramic	Fluorofilm™	PTFE		Pipe 1/2" NPT M	
	25HV	3.0	Polypropylene	316 S.S.	Fluorofilm™	PTFE		PE .5" O.D. Vinyl .938" O.D.	
	25P	3.0	Polypropylene	Ceramic	Fluorofilm™	PTFE		Pipe 1/2" NPT M	
	25T	3.0	Polypropylene	Ceramic	Fluorofilm™	PTFE		PE .5" O.D.	
	26S**	3.0	PVC	Ceramic	Fluorofilm™	Viton®	4FV	PE .5" O.D.	
	27	3.0	316 S.S.	316 S.S.	Fluorofilm™	PTFE		Pipe 1/2" NPT M	
	29	3.0	UHMW PE	Ceramic	Fluorofilm™	Viton®		PE .5" O.D.	

Output Information with Standard Liquid End

Series	Gallons per Hour: Min	Max	Liters per Hour: Min	Max	mL/cc per Minute: Min	Max	mL/cc per Stroke: Min	Max	Maximum Injection Pressure
C10, C70*, C90*	0.001	1.3	0.005	4.9	0.08	82	0.08	0.82	300 psi (20.7 Bar)
C11, C71*, C91*	0.003	2.5	0.010	9.5	0.16	158	0.16	1.58	150 psi (10.3 Bar)
C12, C72*, C92*	0.004	4.0	0.015	15.1	0.25	252	0.25	2.52	100 psi (6.9 Bar)
C13, C73*, C93*	0.008	8.0	0.030	30.0	0.51	505	0.51	5.05	60 psi (4.1 Bar)
C14, C74*, C94*	0.020	20.0	0.076	76.0	1.26	1262	1.26	12.62	25 psi (1.7 Bar)
C76*	0.004	4.0	0.015	15.1	0.25	252	0.25	2.52	175 psi (12.1 Bar)
C77*	0.010	10.0	0.038	38.0	0.63	631	0.63	6.31	80psi (5.5 Bar)
C78*	0.025	25.0	0.095	95.0	1.58	1577	1.58	15.77	30 psi (2.07 Bar)

*Minimum output is based on 1 stroke per minute and 10% stroke setting, minimum output can be reduced further in external mode. Series C9 pumps may be programmed for strokes per hour for lower outputs.

AutoPrime™ Liquid End Configuration Data & Materials of Construction

Drive Assembly	Liquid End No.	Size Code	Head & Fittings	Balls	Liquifram™	Check Valve	Accessory	Tubing & Connections
C11, C71, C91	D60HI	1.8	Acrylic/PVC	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	PE .375" O.D.
C12, C72, C92	D68HI	1.8	PVC/PVC	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	PE .375" O.D.
C13, C73, C93	D10HI	3.0	Acrylic/PVC	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	PE .5" O.D.
	D18HI	3.0	PVC/PVC	Ceramic	Fluorofilm™	PVDF/Polypret®	4FV	PE .5" O.D.

Output Information – AutoPrime™ Liquid Ends (Liquid end models beginning with "D")

Series	Maximum Output: GPH	Liters/hr	mL/cc per minute	mL/cc per stroke	Maximum Pressure: PSI	Bar
C11, C71, C91	2.3	8.7	145.1	1.45	150 psi	10.3
C12, C72, C92	3.8	14.4	239.8	2.40	100 psi	6.9
C13, C73, C93	7.8	29.5	492.2	4.92	60 psi	4.1

AutoPrime™ liquid ends have 3 check valves: suction on the bottom; discharge on the front; and autoprime bleed on the top. By design, a repeatable portion of the process fluid continuously bleeds through the top check valve to be returned to the chemical supply. The result is the assurance that any gas in the head is automatically relieved thus eliminating air-binding. The maximum output per the tables above is reduced to account for the continuous bleed.

☐ See front page for voltage code specifications.

Plastic heads with tubing connection include ½" NPT and ½" BSP.

**These Liquid Ends are available without a 4FV, simply drop the "S" at the end of the Liquid End number to order the model without a 4FV.

#These liquid ends use 3/8" diameter balls. Pump output may be reduced in some applications.

† To specify ¼" NPT male, change 'I' to 'P'.
To specify black, UV resistant tubing, change 'I' to 'U'.
To specify 3FV, change 'S' to 'T'.

3FV indicates that the pump is equipped with an LMI Three Function Valve (pressure relief, priming aid, line drain).

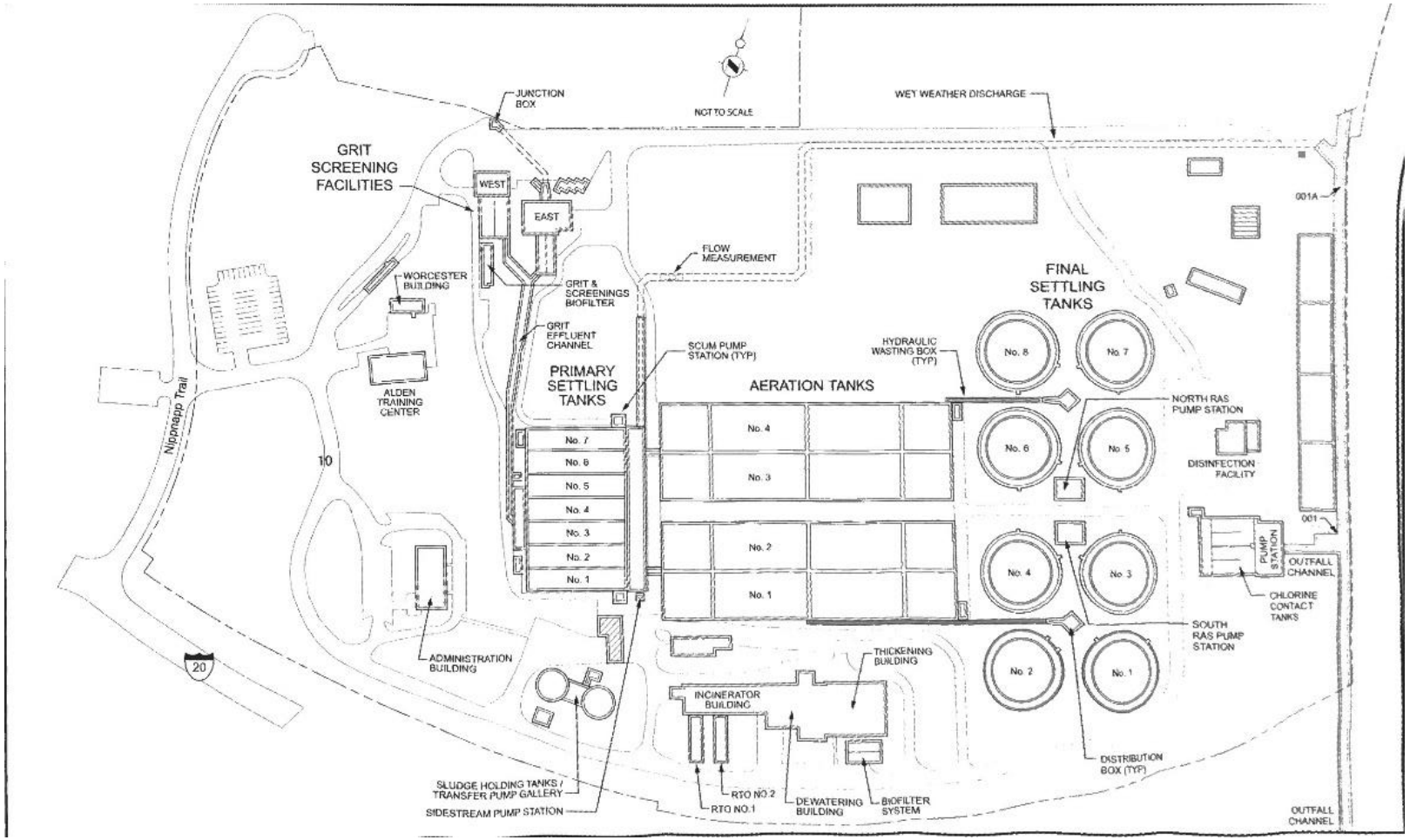
4FV indicates that the pump is equipped with an LMI Four Function Valve. This diaphragm type, anti-syphon/pressure relief valve is installed on the pump head. It provides anti-syphon protection and aids priming, even under pressure.

Fluorofilm™ is a copolymer of PTFE and PFA.
Polypret® is an elastomeric PTFE copolymer.

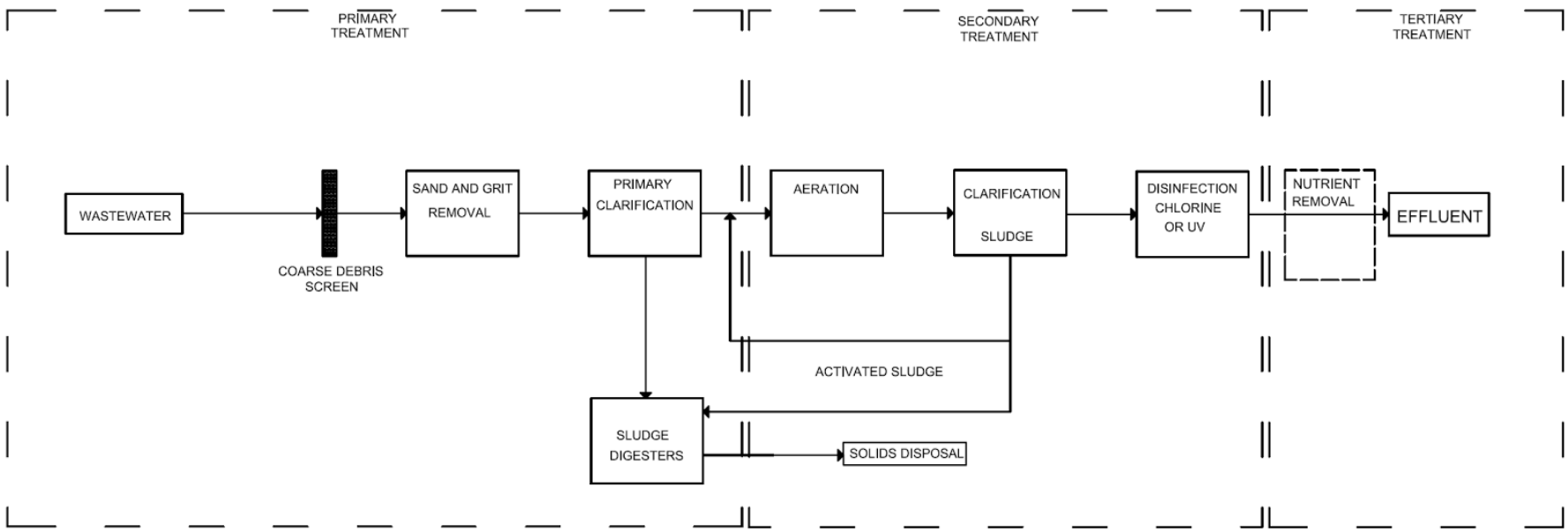
Polypret is a registered trademark of Milton Roy, LLC.

Fluorofilm and Liquifram are trademarks of Milton Roy, LLC.
Viton® is a registered trademark of DuPont.

Appendix F: UBWPAD Schematic



Appendix G: Typical Wastewater Treatment Schematic



Appendix H: Informal Interview with Bobby Young

An informal interview with Bobby Young was completed on October 7, 2015. Bobby Young is an EHS Engineer at MilliporeSigma. Bobby was responsible for setting up a relationship with a wastewater treatment plant (WWTP) located in Connecticut. MilliporeSigma delivers its methanol waste to the WWTP to be reused in the denitrification process. We interviewed him to learn about the process of contacting companies, as well as the general process of transportation and purchase of the desired carbon source.

1. How did you get in contact with the wastewater treatment plant?

I attended a Water Environment Federation Conference and "Beneficial Re-use of Hazardous Substances" was one of the topics. I started randomly contacting WWTPs and eventually partnered w/Veolia Water who operates the Danbury POTW.

2. How do you contact companies to gain alternative carbon sources from them for the wastewater treatment plant?

You have to assure them that the alternative carbon source will be used for experimental purposes, the transport of the material is compliant w/DOT regulations, and that any residual will be managed appropriately.

3. What are the costs associated with the process?

Depending on the distance to the POTW, transportation could be between $300.00 - $500 including miscellaneous charges.

4. Who pays for transportation?

The offerer.

5. How often does the wastewater treatment plant get the methanol?

This is a daily process; 24 hours a day.

6. Can you describe the general process of giving the waste to the plant?

First there is bench top study, the WWTP or their contractors will pay for or complete the study. They will benefit economically from the use of the material. There are recycling permits that have to be completed w/the State you ship from and approval to receive by the State you ship to (if out of state).

7. Did you encounter any obstacles when setting this up?

Out of state approval; long process...

8. Do you have any advice for us when setting up a similar system with the Upper Blackstone wastewater treatment plant?

Do as much research as possible to determine cost of virgin carbons sources, cost for hazardous waste disposal, etc., volume generated, cost savings for WWTP and Generator of Hazardous Waste, and negotiate fair credit to Generator compared to cost savings by WWTP.